CATALYSIS

E. JOBLING

SECOND EDITION

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TEXT-BOOKS OF CHEMICAL RESEARCH AND ENGINEERING

CATALYSIS

AND ITS

INDUSTRIAL APPLICATIONS

BY

E. JOBLING, M.C.,

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PREFACE

SINCE the publication of the first edition, the subject of Catalysis has undergone most extensive development. For this reason and because the first edition went to press unrevised and incomplete owing to the author's absence on active service, very considerable alterations have been necessary for the second edition. In many places the subject-matter has been entirely rewritten, whilst two further chapters have been added. A number of references are now included for the assistance of readers desirous of obtaining fuller details of the various phases of the subject.

The author wishes to express his thanks to Mr. T. Beacall, B.A. (Cantab), both for his assistance in connection with Chapter 8, and for the many valuable suggestions which he has been kind enough to make in reading through the MS.

E. J.

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ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATION.	PUBLICATION.
Annalen	Justus Liebig's *Annalen der Chemie.*
Ann. Chim. Phys.	*Annales de Chimie et de Physique.*
B. P.	British Patent.
Ber.	*Berichte der Deutschen chemischen Gesellschaft.*
Brit. Ass. Rep.	Report of the British Association for the Advancement of Science.
Can. Chem. J.	*Canadian Chemical Journal.*
Chem. Met. Eng.	*Chemical and Metallurgical Engineering.*
Chem. News.	*Chemical News.*
Chem. World	*Chemical World.*
Compt. rend..	*Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.*
D. R. P.	Deutsches Reichs-Patent.
Fr. P.	French Patent.
Int. Con. App. Chem.	International Congress of Applied Chemistry.
J. Chem. Soc.	*Journal of the Chemical Society.*
J. Franklin Inst.	*Journal of the Franklin Institute.*
J. Gas Lighting	*Journal of Gas Lighting.*
J. Ind. Eng. Chem.	*Journal of Industrial and Engineering Chemistry.*
J. Inst. Pet. Tech..	*Journal of the Institution of Petroleum Technologists.*
J. pr. Chem..	*Journal für praktische Chemie.*
J. Roy. Soc. Arts	*Journal of the Royal Society of Arts.*
J. Russ. Phys. Chem. Soc.	*Journal of the Physical and Chemical Society of Russia.*
J. Soc. Chem. Ind.	*Journal of the Society of Chemical Industry.*
Jahresber.	*Jahresberichte über die Fortschritte der Chemie.*
Phil. Trans.	*Philosophical Transactions of the Royal Society of London.*
R. P. C.	Reports of Patent, Design, Trade Mark, and other Cases.
U. S. P.	United States Patent.
Zeitsch. angew. Chem.	*Zeitschrift für angewandte Chemie.*
Zeitsch. anorg. Chem.	*Zeitschrift für anorganische Chemie.*
Zeitsch. Elektrochem.	*Zeitschrift für Elektrochemie.*
Zeitsch. physikal. Chem..	*Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.*

NOTE.

All temperatures throughout the book are in Centigrade.

Catalysis and its Industrial Applications.

CHAPTER I.

Introduction.

1. It is a matter of common observation that many chemical reactions which normally proceed slowly, often so slowly as to be overlooked, can be accelerated to a greater or less degree by the introduction of some foreign material. The importance of this phenomenon—defined as far back as 1835 by Berzelius [1] as Catalytic—will at once be evident, for it affords the technologist a powerful means by which to effect reactions which would otherwise be economically impossible.

Nearly twenty years ago, Ostwald [2] predicted that the great advances of chemical industry would be made by means of the more extensive employment of catalytic agencies. It is left for the reader to judge whether this prophecy has been fulfilled. Moreover, the attention which the subject is receiving nowadays at the hands of industrial chemists justifies the hope of still more valuable application in the future.

General Considerations.

2. We have seen that catalysis is associated with an alteration in the speed of a chemical reaction. But catalysis is not unique in this respect, for there are other factors which exert a similar effect. If the velocity of a reaction be expressed in the following terms :—

$$\text{reaction velocity} = \frac{\text{chemical force}}{\text{chemical resistance}},$$

then it follows that any alteration in either the chemical force or the chemical resistance will correspondingly affect the reaction velocity. Thus, the addition of heat will at the same time increase the chemical force and decrease the chemical resistance, leading thereby to an appreciable increase in the reaction velocity. Increasing the viscosity, on the other hand, will lower the reaction velocity by increasing the chemical resistance. The effect of other constraining factors might be determined in a similar manner.

The influence of the factors just mentioned is small, however, in comparison with that of a good catalytic agent, for by the use of materials of this nature the chemical resistance may be reduced to such a marked degree that in many cases it becomes unnecessary to increase the chemical force by the expenditure of extraneous energy in order to accelerate an impracticably slow reaction to the point of commercial utility.

3. So far we have been dealing with the simple question of a reaction which proceeds to completion. But catalysis is not concerned so much with these as with reactions which, like the saponification of fats, proceed in a leisurely manner and never attain completion. Such reactions are reversible, for they come to a stop as the result of interaction between the final products. There are, therefore, two reaction

velocities to be considered, one for the direct and one for the inverse reaction.

As we shall see later, a catalyst affects both reaction velocities to the same extent, from which it follows that the final state of equilibrium in a reversible reaction is unaltered by the presence of a catalyst. With the other factors of temperature, pressure, and concentration, this is not the case. Any change in these conditions alters to a different extent the velocities of the direct and inverse reactions and thereby shifts the point of equilibrium.

4. Whilst we are primarily concerned here with the bearing of catalysis upon industrial reactions, we cannot afford to overlook the influence of the factors just mentioned, for they figure very prominently in modern practice, particularly in connection with gaseous reactions.

First, then, it will be advisable to consider the influence upon the final state of equilibrium of each of these factors in turn.

Influence of the Concentration.

5. The effect of varying the concentration of any one constituent of a reversible reaction can be determined by the application of the law of Mass Action. According to this well-known law, the amount of chemical change taking place in a reaction is dependent upon the molecular concentration of each constituent.

One way, therefore, in which a reversible reaction may be forced nearer completion in any one direction is by the use of an excess of one of the components contributing to the reaction in that direction. The effect is not very noticeable unless a very considerable excess is used, and even then it does not modify the reverse reaction in the slightest. A more effective method of furthering the forward reaction consists in removing one of the products as soon as it is formed,

for no reverse reaction can then set in to diminish the yield.

6. With regard to the factors of temperature and pressure, their influence can best be determined by the aid of Le Chatelier's law, which expresses the general principle of resistance to change. This law, which is a deduction from thermodynamical reasoning, states in effect that if a system which is in equilibrium be subject to some change (e.g., by altering the temperature or the pressure), the equilibrium will be displaced in that direction which tends to oppose the effect of the change.

Many attempts have been made to work out mathematically the relation between the reaction velocity and the temperature or pressure. For these quantitative relationships the reader is referred to such books as :—

" Applications of Thermodynamics to Chemistry " —Nernst (1907).

" Thermodynamics of Technical Gas Reactions " —Haber (1908).

" A System of Physical Chemistry "—Lewis (1918).

But for the purpose of the present work, the qualitative deductions will be sufficient.

Influence of the Temperature.

7. By a restatement of the above-mentioned law of Le Chatelier in terms of temperature, we get that any change in the temperature of a system in a state of equilibrium is followed by a reverse chemical change within the system. This, however, is van't Hoff's " principle of mobile equilibrium," which is thus seen to be but the restricted application of a wider law.

Now there are two types of reactions to be considered, viz., exothermic and endothermic reactions,

the former being accompanied by an evolution of heat, the latter by an absorption. Obviously, if the forward reaction is exothermic, then the reverse reaction must be endothermic.

Take exothermic reactions first. The addition of heat in these cases will cause an increase in those products which are formed with absorption of heat; in other words, it favours the reverse reaction, so that the rise in temperature will be detrimental to the yield of the direct reaction. With endothermic reactions, the contrary is the case. Increasing the temperature now favours the formation of the products of the forward reaction.

From this it will be seen that the direction of the shifting of the equilibrium in a reversible reaction caused by an alteration in the temperature can be predicted if the thermal value of the reaction is known.

Influence of the Pressure.

8. In the same way that van't Hoff's law has just been seen to be the temperature application of Le Chatelier's law, so Robin's law is the pressure application of the same principle. Robin's law states that raising the pressure favours the system formed with a decrease in volume, whilst diminishing the pressure favours the system which has the greater volume.

Consider, for instance, the union of nitrogen and hydrogen to form gaseous ammonia.

$$N_2 \text{ (two vols.)} + 3\,H_2 \text{ (six vols.)} \rightleftarrows 2\,NH_3 \text{ (four vols.)}.$$

From this equation it is apparent that, since eight volumes of nitrogen-hydrogen mixture form only four volumes of ammonia, the reaction is accompanied by a diminution in volume. According to Robin's law, then, an increase of pressure should further the formation of ammonia, a prediction which is borne out by experiment.

Definition.

9. Of the many definitions of the term " catalyst," that of Ostwald,[3] by reason perhaps of its authoritativeness, has obtained general acceptance. This definition states that *a catalytic agent is that material which affects the velocity of a chemical reaction without appearing in the final products.*

10. From the definition just set forth, it is evident that the effect of a catalyst may be either positive or negative, i.e., the catalyst may either accelerate or retard the reaction. Practically all catalysts fall into the first or positive class, but there are a few which effect what is known as *Negative Catalysis.* The phenomenon is to be observed in the case of a substance which is added to another in order to preserve it, as when a little alcohol is added to chloroform to retard its decomposition under the influence of air and light. When carefully differentiated, however, from the paralysing effect which certain bodies exert upon positive catalysts (see section 15), the importance of negative catalysis dwindles into insignificance.

We come now to a consideration of the criteria of catalytic processes.

Characteristics of Catalysts.

(1) *Unchangeableness of the Catalyst.*

11. That the catalyst has the same chemical composition at the end as at the beginning of the reaction is undoubtedly the most essential characteristic of catalytic phenomena. Very often the catalyst is known to participate directly in the reaction, but in these cases, though the equations of the intermediate stages involve the catalyst, the *gross* equation must not do so.

In a good many instances, the catalyst is found to emerge from the reaction in an altered *physical* state

—incidentally proving thereby that it has taken an active part in the reaction. For instance, the crystalline variety of manganese dioxide, used as a catalyst in the decomposition of potassium chlorate, finishes as a fine powder; and a curious alteration in the surface of the catalyst occurs in the case of the platinum [4] of the ammonia-oxidation process, or of silver [5] when employed in the surface-combustion process. In these instances the catalyst has to mature before attaining its maximum activity, this "ageing," as it is called, consisting most probably of a physical devolution into a fineness of division greater than can be obtained by mechanical means. It should be observed, nevertheless, that the variation of energy produced by the change can hardly modify the reaction to any appreciable extent.

(2) *Amount of Catalyst Necessary.*

12. *The Amount is Small.*—Reasoning from the statement in Ostwald's definition that the catalyst is not found in the final products of a reaction, it follows that the catalyst ought to be able to function repeatedly and indefinitely, and consequently a minimum quantity should suffice. And in practice it is the case that only a trace of the foreign material, often in fact but an infinitesimal amount, is sufficient to effect the transformation of indefinitely large quantities of the reacting substances. For example, one milligram of colloidal platinum will bring about the combination of many litres of hydrogen and oxygen without the activity of the catalyst becoming impaired.

The necessity for a mere trace of the added material ought to be regarded as one of the most important attributes of truly catalytic processes. There are instances in which the solvent, a third and unchanging body, varies the velocity of the reaction between two substances dissolved therein, and such

an effect might be regarded as catalytic, were not exception taken, and rightly so, to the large amount of the third substance necessary.

13. *The Amount remains Constant.*—Theoretically, the quantity of the catalyst should of course remain unchanged. In practice, however, even in the absence of secondary reactions, which are often a source of loss, renewal of the catalytic agent becomes necessary at intervals, largely on account of deterioration consequent upon the accumulation of " poisonous " material—a matter which will be referred to more fully later on. For this reason, it is customary to refer to the " life " of a catalyst, meaning thereby the period over which the catalyst retains a reasonable activity.

Instances of true catalysis are known in which the catalyst either increases or decreases in quantity as the reaction proceeds, the apparent contradiction arising from the fact that the catalyst, positive or negative, is set free as one of the reaction products. The phenomenon is known as *Auto-catalysis.* An example is found in the hydrolysis of an ester by water, where the liberated acid acts as the catalyst. Cases of negative auto-catalysis, or *auto-retardation,* are rare, and are only to be found in chemical literature.

(3) *Effect upon the Final State of Equilibrium.*

14. The difference in the energy equations of the initial and final states of a reaction represents the amount of energy transformed, and since a catalyst introduces no energy, it follows that the final state of equilibrium must remain unaffected. Otherwise, of course, by permitting the reaction to take place alternately with and without the assistance of a catalyst, energy could be generated and a perpetual motor established.

Again, the final state of equilibrium of a reversible

reaction depends only upon the ratio of the velocities of the two inverse reactions, and as this final state has been shown to remain unaltered by the introduction of a catalyst, it may be deduced that the catalyst affects the two reaction velocities to the same extent.

As a further deduction from the same statement that the final state of equilibrium is independent of the catalyst, it may be observed that the state of equilibrium must necessarily be independent of both the nature and the quantity of the catalyst. Thus, in the case of the Contact process for sulphuric acid, it is not the equilibrium but only the velocity of its attainment which is affected by the use of vanadium pentoxide or ferric oxide instead of platinum.

(4) *Effect of Additional Substances upon Catalysts.*

15. *Poisons.*—It is a curious and important fact that the activity of a catalyst is liable to be greatly diminished by the presence of another substance, of which even a trace is often sufficient to paralyse the catalyst. The classic instance of such an *anti-catalyst* or *poison*, as the contaminating substance is called, is taken from the manufacture of sulphuric acid by the Contact process, where at the very outset it was found that the platinum asbestos employed for the oxidation of sulphur dioxide deteriorated so quickly as to render the process unworkable. Happily, the threatened ruin of this industry was averted by the discovery that it was the arsenic and other impurities contained in the sulphur dioxide which clogged the pores of the platinum and accounted for its diminished activity. Similarly, in the synthesis of ammonia by Haber, the presence of poisons contributed greatly to the difficulties involved in the establishment of the process on a commercial basis.

In all cases, the effect is remarkable for the

smallness of the quantity of the poison capable of rendering the catalyst inactive. In the last-mentioned process, for instance, the iron used as catalyst becomes quite " dead " when it contains $\frac{1}{10}$ % sulphur, and is of little use even with $\frac{1}{100}$ % impurity.

Arsenic seems to paralyse the action of most catalysts, and the same applies more or less to hydrocyanic acid, mercuric chloride, iodine, etc. Each catalyst, however, has its own list of poisons. Some of the poisons for the iron of Haber's synthesis, strangely enough, are of quite a different nature from those of the platinum in the sulphuric acid manufacture. In some cases, especially when the inhibitor is oxidisable, the catalyst may be made to recover its activity; in other cases, the catalyst must be discarded or its paralysis prevented by the careful purification of the reacting materials.

Enzymes, which are also catalysts, are subject to a similar inhibiting influence, often by the same substances that poison purely " inorganic " catalysts.

The action of catalytic poisons should not be confused with that of negative catalysts. In the latter case it is the reaction which is retarded, whereas in the former the catalyst has its activity reduced.

16. *Promoters.* — In contradistinction to the above-mentioned inhibiting effect, other substances have been observed to increase the activity of a catalyst when they are added in minute quantity. Thus, practically all metallic catalysts become activated when certain oxides or compounds of other metals, or even the other metals themselves, are distributed through them. In Haber's synthetic ammonia manufacture, for instance, the activity of the iron employed as catalyst is quickened to a very useful extent by the presence of a trace of such a foreign body as potash. Further research in connection with *promoters*, as they are called, would be

amply repaid, for as yet our knowledge is limited to a certain number of isolated facts.

17. When the additional substance does not help to catalyse the main reaction, but rather assists the production of the catalyst, the phenomenon has been referred to as *Pseudo-catalysis*.

A pseudo-catalyst, then, accelerates the production of an auto-catalyst, but does not accelerate the main reaction. A technical example is furnished by the drying of linseed oil, where the addition of a so-called siccative, such as the oxide of manganese, of lead, or of zinc, is found to hasten the process, probably by accelerating the development of the peroxide-like substances which determine the drying.

18. It may be noticed here that the joint effect of two catalysts need not necessarily be the sum of the effects of each catalyst taken separately. Though this does sometimes hold, the joint effect is more often greater and only occasionally less.

19. *Contact-carriers.* — To obtain the greatest efficiency from a catalyst, it should present as large a surface as possible to the reacting components. For this reason, it should preferably be spread over a bed or support of an indifferent porous material such as asbestos, fireclay, kieselguhr, or pumice stone. The supporting material is known as a " contact-carrier," and its use finds wide application in technical processes, more especially when the catalyst is a costly metal.

(5) *Specific Activity of Catalysts.*

20. As Ostwald has pointed out, there is probably no kind of chemical reaction which cannot be influenced catalytically, and no substance which cannot act as a catalyst. Yet each reaction requires its own specific catalyst or catalysts. Take, for example, the case of the decomposition of alcohols by heat. Some catalysts, e.g., thoria, catalyse the dehydration

process which produces ethylene hydrocarbons; whereas with other catalysts, such as finely-divided copper, it is the formation of aldehydes and ketones by dehydrogenation which is accelerated.

Of course, under Armstrong's theory,[6] the presence of water or some other electrolyte is essential to all chemical reactions, but experiment is against this generalisation. Still, there are particular substances, such as platinum and nickel, which appear capable of manifold application in a catalytic capacity, as the following pages will show. But whilst the behaviour of these substances is an argument against absolute specificity of action, the fact remains that it cannot safely be predicted what will happen in any case not already tested by experiment.

Occasionally, the discovery of a catalyst is a matter of accident or good fortune, as in the case of the synthesis of indigo, where the accidental breakage of a thermometer liberated the catalytic material (mercury), which rendered practicable the most obstinate reaction of the process. More generally, however, before the commercial success of a catalytic process can be assured, a large amount of systematic scientific research has to be undertaken embracing all manner of likely catalysts.

False Catalysis.

21. We have had occasion to refer in this chapter to certain reactions classified as auto-catalytic and pseudo-catalytic. There exists another class of chemical reactions, known as *Induced Reactions*,[7] in which a slow reaction between two substances is accelerated in the presence of a simultaneous rapid reaction between one of the reacting bodies of the first reaction and a third body. The third body, therefore, acts in a manner which suggests catalysis. As, however, these reactions are of no technical importance, it is unnecessary to discuss them further.

22. The mention of other classes of reactions bordering upon the catalytic raises the question as to the exact line of demarcation between catalytic and non-catalytic processes. As a matter of fact, it is very difficult, if not impossible, to draw such a line. In any doubtful case which may come under consideration, it is well to fall back upon the definition, and, failing that, upon the characteristics which have been under discussion.

The Weldon process, for instance, would be relegated to the class of *False Catalysis*, for though manganese dioxide there plays the part of a third and necessary agent in the oxidation of hydrochloric acid, it is not employed in the presence of both of the reacting bodies, and cannot be considered, therefore, as accelerating their direct combination. The same applies to other cyclic processes, such as the Messerschmidt process for hydrogen manufacture, or the process for the removal of hydrogen sulphide from illuminating gas by the use of ferric oxide or manganese dioxide. Then, again, it would be incorrect to speak of those reactions which involve the use of so-called " condensing agents " as being catalytic reactions. True, the addition of a small quantity of such an agent may determine the success of the reaction, but only by combining with one of the products and thereby preventing the annulling effect of the reverse reaction.

Classification of Catalysts.

23. For the purpose of convenience, catalytic agents may be broadly divided into three classes :—

(1) Chemical agents, which function by means of intermediate reactions. The substances known as " carriers " (halogen-carriers, for instance, and not the contact-carriers already referred to) fall into this class.

(2) Physical agents, such as hot surfaces, colloidal solutions, etc., in which the effect is dependent upon surface tension, occlusion, diffusion, or other physical phenomenon.

(3) Indeterminates, which appear to combine the above two functions to a greater or less degree. Some of the finely-divided metals may be regarded as belonging to this category.

A classification of this kind is naturally only a provisional one, for it is not certain in any case exactly how the catalyst does function. There are many who regard the physical agents as being quasi-catalytic in effect, and consider as true catalysts only those bodies which exert their influence by participating in the reaction. Be that as it may, this classification is as good as our present ignorance of the theory of catalytic action permits. If the reader desires further information as to the various theories which have so far been put forward, reference should be made to :—

" A System of Physical Chemistry " (Vol. I.)—Lewis (1918).

" Catalysis in Theory and Practice "—Rideal and Taylor (1919).

" Chemical Statics and Dynamics "—Mellor (1904).

REFERENCES FOR CHAPTER I.

[1] *Jahresber.*, 1836, *15*, 237.
[2] *Zeitsch. Elektrochem.*, 1901, *7*, 995.
[3] See page 298, " Outlines of General Chemistry "—Ostwald (1912).
[4] See the photomicrographs reproduced opposite to page 97 of " Catalysis in Theory and Practice "—Rideal and Taylor (1919).
[5] See the photomicrographs reproduced opposite to page 448 of " Coal and its Scientific Uses "—Bone (1918).
[6] See Baker, *J. Chem. Soc.*, 1902, *81*, 400.
[7] " Die induzierten Reaktionen " (*Sammlung chem. und chem.-techn. Vorträge, Bd.* 13)—Skrabal (1908).

BIBLIOGRAPHY.

" Catalysis in Theory and Practice "—Rideal and Taylor (1919).
" Catalysis in Industrial Chemistry "—Henderson (1919).
" La Catalyse en Chimie Organique "—Sabatier (1913).
" Die Katalyse " (Vol. I.)—Woker (1910).

CHAPTER II.

Sulphuric Acid Manufacture.

1. As examples of the application of catalysis to industrial chemistry, the two methods for the manufacture of sulphuric acid deserve first mention —the Chamber process as an illustration of the first class of catalytic action referred to in Chapter I, and the Contact process as illustrative of the second.

In each case the atmospheric oxidation of sulphur dioxide is the primary reaction involved. Now, at ordinary temperatures, and then only in solution, sulphur dioxide is oxidised with extreme slowness, while even at the temperatures which obtain during the roasting of pyrites the reaction only takes place to a small extent. For accelerating the oxidation two separate methods are available, the first or Chamber process based upon the capacity of oxides of nitrogen for serving as " carriers " of atmospheric oxygen to sulphur dioxide when in aqueous solution, and the second—the Contact process—upon the property of platinum and other " contact " bodies to induce the rapid formation of sulphuric anhydride in a gaseous mixture of sulphur dioxide and oxygen. Each of these methods will be dealt with from the catalytic point of view.

I. Chamber Process.

2. The oxides of nitrogen function as true catalysts for this process, since they can be recovered unchanged from the products of the reaction and

utilised repeatedly for accelerating the oxidation of further quantities of sulphur dioxide. Consequently, a Chamber plant includes arrangements for recovering the nitrogen oxides from the exit gases of the leaden chambers in which the oxidation of the sulphur dioxide has taken place and for reintroducing the same into the apparatus.

3. The cycle of operations is briefly this: The hot gases from the brimstone or pyrites burners, containing about 7% sulphur dioxide, are made to take up oxides of nitrogen by being brought into contact in a Glover tower with a solution of nitrosyl sulphuric acid, i.e., sulphuric acid which has absorbed the nitrogen oxides of a previous operation. The gaseous mixture is then passed through a series of leaden chambers, into which steam is forced or dilute sulphuric acid sprayed, for the completion of the reaction and the deposition of the resulting acid. After playing their catalytic *rôle*, the nitrous gases emerging from the last chamber are absorbed by sulphuric acid in a Gay-Lussac tower, forming nitrous vitriol, which is then transferred to the Glover tower for the reintroduction of its contained nitrous gases into fresh burner mixture.

In the most carefully conducted systems a loss of nitrous fumes occurs—averaging 3 to 4 parts of nitre per 100 parts of sulphur burnt—and this has to be made good, usually by the periodic addition of nitric acid at some point of the cycle. The older English method is to introduce an iron pot containing nitre and sulphuric acid into the burner gas flue. More recently, the nitre pots have been replaced by a simple ammonia-oxidation apparatus (see Chapter IV, section 16) for supplying the oxides of nitrogen required. On the Continent it is the practice to add liquid nitric acid to the nitrous vitriol of the Glover tower, or to spray liquid nitric acid or a solution of sodium nitrate into the lead chamber.

4. The theory of the process has engaged the attention of chemists for upwards of a century. Many nitrogen complexes, apparently easily interchangeable, are formed by the interaction of nitrogen oxides, sulphuric acid, water and oxygen, and though, for the sake of convenience, nitric acid may be referred to as the catalyst, it is probably one of the above-mentioned bodies which really functions in this way. The various theories[1] advanced by Lunge, Raschig, Divers, and others, apparently differ from each other only in their conception of this intermediate compound or compounds.

There is no question, however, that the reaction proceeds in any other way than by means of "intermediate reactions." Taking a simple view of the reactions involved, the instantaneous formation of "chamber crystals" (nitrosyl sulphuric acid) from sulphur dioxide, nitrous vapours and oxygen provides a common lecture experiment, as also the equally instantaneous decomposition of these crystals when brought into contact with water. By the postulation, then, of the intermediate formation of "chamber crystals," the mystery surrounding the acceleration of the normally slow reaction between sulphur dioxide, water and oxygen by the agency of nitric oxide finds a plausible solution; though, of course, the problem is not such a simple one as this.

5. The Chamber process is an old-established one —its inception dating back to the middle of the eighteenth century—but with the aid of modern developments, such as Falding's high chambers, Opl towers, and Gaillard concentrators, it is still able to compete successfully with the rival Contact method. As a matter of fact, more sulphuric acid is made by the Chamber process than by the Contact process, even in countries such as Germany where the Contact method has been largely introduced.

II. Contact Process.

6. The catalytic activity of platinum in promoting the union of sulphur dioxide and oxygen was made the subject of a patent as long ago as 1831 by Phillips,[2] but the successful utilisation of the fact upon an industrial basis is a matter only of comparatively recent years. The protracted development is accounted for by the many difficulties encountered, difficulties arising largely from the inadequacy of contemporary engineering chemistry. Now that these obstacles have been overcome, full technical success is assured, and the process has already displaced the older Chamber process in the manufacture of the more concentrated acid; whilst for the production of oleum or fuming sulphuric acid so essential to the dye and explosive industries, this process is the only one available.

The most serious difficulties in the successful working of the process were concerned with the regulation of the temperature and the prevention of the gradual destruction of the catalytic power of the platinum.

7. The reaction—

$$SO_2 + O \rightleftarrows SO_3$$

is accompanied by the evolution of 22,600 calories, a quantity sufficient to damage irreparably the contact material unless precautions are taken. Of course, with the diluted burner gas mixture—and the law of mass action demands an excess of oxygen if anything approaching a quantitative conversion into sulphuric anhydride is to be obtained—the effect of the heat developed is not so great, yet it is still enough to raise the temperature above that for obtaining the best results.

8. The influence of the temperature upon the reaction was, among other things, investigated by

Knietsch [3] of the Badische Anilin und Soda Fabrik, and his results in this connection, published in 1901, are indicated by Figs. 1 and 2. Technical burner gas, containing 7% sulphur dioxide, 10% oxygen, and the rest nitrogen (corresponding to about $2SO_2 : 3O_2$), was passed at varying rates over platinised asbestos heated to different temperatures, and it was observed (see curve 1, Fig. 1) that the reaction began at about 200° and reached approxi-

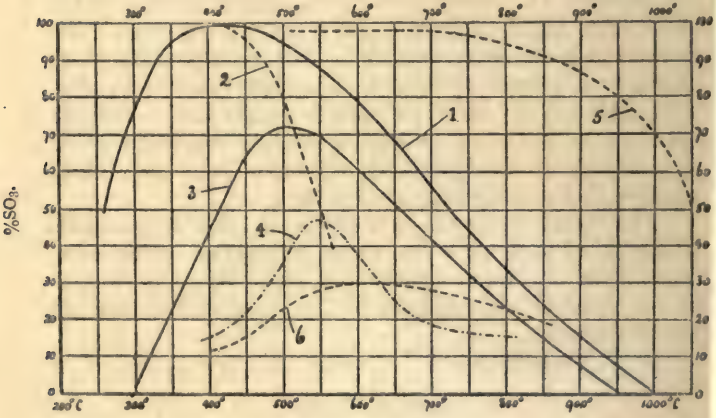

FIG. 1.

mate completion at 420°, whilst above this temperature the yield of sulphuric anhydride gradually fell off until at 1000° no reaction was possible. By increasing the rate of flow, the temperature of maximum conversion increases, but at the same time the maximum yield diminishes. This is clearly shown by curve 2, Fig. 1, which traces the loci of the maxima for the curves representing faster rates of flow. Curve 3, Fig. 1, is an example of such a curve, the speed in this case being 30,000 c.c. per minute,

which is 100 times as fast as that involved in curve 1.

In Fig. 2 the influence of the temperature upon the reaction is plotted against the rate of flow of the gases, or what amounts to the same thing, against the quantity of platinum employed. The steepness of the curves as they leave zero should be noticed, for they point to the fact that a violent reaction ensues when the roaster gases first come into contact with

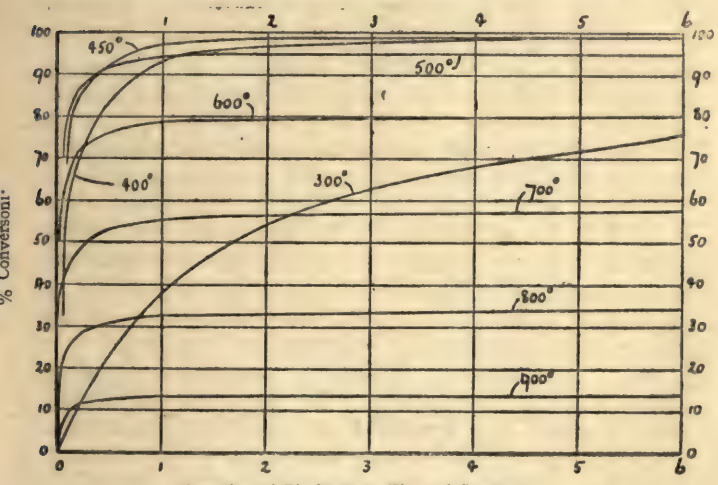

FIG. 2.

the catalyst—from which may be anticipated a danger from intense local heating.

It is evident from these curves that, with platinum as the catalytic agent, the most desirable temperature lies at about 420°. A higher temperature would increase the velocity of formation of sulphur trioxide, but at the same time detrimentally affect the equilibrium. And since rapidity of production is always essential to the success of a manufacturing process, a compromise is usually effected, in this case

at or somewhat above 450°. It may be mentioned that under the best conditions a yield of sulphuric anhydride can be obtained of over 98% of that theoretically possible.

To maintain the contact mass at the desired temperature, some external cooling is necessary; and this is generally brought about by causing the comparatively cool burner gases to flow round the tubes in the converter which contain the contact material. The temperature of the ingoing gases is raised thereby to about 300° by means of heat extracted from the contact reaction. Superheating at the beginning of the reaction has to be avoided, either by bringing the burner gases into contact with material of gradually increasing richness in platinum,[4] or by effecting the reaction in separate stages in different converters, the sulphuric anhydride contained in the gases leaving the first converter being absorbed before passing the gases into the second.[5] In any case, the reaction temperature should be so maintained that the temperature of the gases leaving the contact material lies between 400° and 450°.

9. The remaining difficulty, that of the gradual diminution in the efficacy of the platinum employed, is one which has troubled manufacturers from the very beginning. As before, the cause of the diminution was located by the researches of the Badische firm, and found to reside in the accumulation in the contact material of "poisonous" substances arising from the impurities contained in the burner gases. In Chapter I it was mentioned that mere traces of these poisons act detrimentally upon the activity of the catalyst, and contact platinum is a case in point, for the presence of 1 to 2% of arsenic compounds was found to render it completely inactive. Crude burner gases contain, in addition to moisture, both gaseous and suspended impurities, the most injurious among which from the catalytic point of view are arsenic,

phosphorus, and mercury, with their compounds. The presence of a trace of water, strangely enough, was found to be essential to the reaction, though in greater quantities water had an injurious effect.

To remove objection on this ground to the use of platinum as contact material, the burner gases are subjected to purification before being introduced into the converter. This is a simple matter as regards the greater quantity of the impurities present in the gases, but unfortunately the last traces are found to resist removal very tenaciously. In a modern plant, purification is effected by first treating the gases leaving the burners with a jet of steam, then by cooling and washing, and finally by passage through sulphuric acid to remove all water but that sufficient to promulgate the reaction. Optical and chemical examination should then indicate the complete absence of impurity.

10. Owing to the cost of purification, as well as to the high price of platinum, the use of other contact material is now finding application. Ferric oxide [6] appears to be the most promising of these, for, apart from its cheapness which permits of repeated replacement, its activity is not liable to the same degree of enfeeblement as is that of platinum. Arsenic compounds, for instance, combine with it to form a non-volatile substance whose presence only slowly reduces the activity. Moisture appears to have the most deleterious effect, and the burner gases are therefore just dried before being introduced into the converter. It might be noticed that arsenic pentoxide,[7] free from iron, itself possesses good catalytic powers for this reaction.

The great disadvantage of ferric oxide lies in the fact that quantitative conversion of sulphur dioxide into sulphuric anhydride cannot be obtained by its aid. This is brought out by curve 4, Fig. 1, which

represents the yields obtained at various temperatures when pyrites cinders were employed as the contact agent. From this curve it will be seen that the maximum conversion does not quite attain 50% (under modern conditions the yield does not rise much above 60%), and then at a temperature over 100° higher than is requisite for platinum as contact material. The fact, however, that the optimum temperature for ferric oxide is higher than for platinum is really no disadvantage, because at the higher temperature the reaction velocity is far greater, and this allows of a more rapid producton of sulphur trioxide. Ferric oxide finds its proper sphere of usefulness when employed in conjunction with platinum, the former being used for the first stage of the operation at high temperatures, giving a 60—65% conversion, and then, after absorption of the resulting sulphur trioxide, employing the latter to complete the reaction at a lower temperature (Mannheim process [8]).

Incidentally, attention is drawn to curve 5, Fig. 1, which shows the effect of heat upon sulphuric anhydride in an empty porcelain tube, that is to say, out of contact with the catalytic material. The remarkable deduction can be drawn from it that sulphuric anhydride, once formed, is very stable at quite high temperatures when contact substances are absent. Complete dissociation is only attained at 1,200°. Curve 6 summarises the results when pieces of porcelain were used as the contact material.

11. Investigators have been busy in recent years seeking still other catalysts for the Contact process, and from the number which have been patented, the discovery of a catalyst would appear to be no difficult matter. For example, vanadic acid [9] or one of its salts, particularly silver vanadate,[10] has strong catalytic properties. In addition, the oxides and

sulphates of chromium, manganese, and copper [11]: the oxides of the rare earths [12]: alloys of different kinds, such as alloys of iron with molybdenum, chromium, or vanadium [13]: are numbered in the list of catalysts. If necessary, any of the substances may be supported upon a carrier of an indifferent material, or may be incorporated with a body which exerts a promoting effect. Nevertheless, so far as is known—and most factories maintain great secrecy upon this and similar matters—the only catalysts in practical use are:—(1) platinised asbestos (Badische [14] and Tentelew [15] processes), (2) platinised magnesium sulphate, made by soaking magnesium sulphate in a solution of a platinum salt and then heating in an atmosphere of sulphur dioxide (Schröder-Grillo [16] process), and (3) burnt pyrites cinders, which are composed of ferric oxide containing a little copper oxide (Mannheim [17] or Clemm and Hasenbach process).

12. With regard to the theory of this reaction but little can be said. Platinum is usually regarded as belonging to the second class of catalyst, viz., those which exert their influence by reason of the occlusion, or condensation upon their surface, of the reacting gases. Some doubt, however, as to the correctness of this belief is raised by a consideration of the numerous other catalysts above referred to, for many are seen to be compounds of metals of dual valency whose action may depend upon the reduction of the higher form of oxidation at the same time that the lower is being oxidised. Ferric oxide would appear to belong to this class. But as an explanation on these lines would presuppose the existence of a hypothetical platinum dioxide, it would be better to argue from the well-authenticated influence of the fineness of division of a substance upon the acceleration of a reaction that the activity of platinum, at least, is more physical than chemical.

REFERENCES FOR CHAPTER II.

[1] Jobling, *Chem. World*, 1912, *1*, 339.
[2] B. P., 6096/1831.
[3] *Ber.*, 1901, *34*, 4069.
[4] B. P., 16254/1900 (Raynaud).
[5] B. P., 2368/1901 (Farbwerke).
[6] B. P., 17266/1898 (Verein Chemischer Fabriken).
[7] Lunge and Reinhardt—*Zeitsch. angew. Chem.*, 1904, 1041.
[8] B. P., 24748/1899 (Verein Chemischer Fabriken).
[9] B. P., 23541/1913 (Badische).
[10] B. P., 15165/1913 (Farbenfabriken).
[11] B. P., 4610/1901 (Verein Chemische Fabriken).
[12] B. P., 1385/1901 (Farbwerke).
[13] D. R. P., 274345 (Classen).
[14] First B. Ps., 15947–50/1898.
[15] First B. P., 11969/1902.
[16] First B. P., 25158/1898.
[17] First B. P., 17266/1898 (Verein Chemische Fabriken, of Mannheim).

BIBLIOGRAPHY.

" Sulphuric Acid and Alkali " (Vol. I.)—Lunge (1913).
" The Alkali Industry "—Partington (1918).

CHAPTER III.

Industrial Chlorine, Salt-Cake Manufacture, Sulphur Recovery.

1. Before proceeding to a discussion of the newer applications of catalysis in the field of inorganic chemistry, reference must first be made to the processes underlying several old and well-known industries which possess great interest when viewed from our present standpoint.

I. Deacon Process.

2. For three-quarters of a century, it has been known that a mixture of hydrochloric acid gas and oxygen, when strongly heated and particularly when in contact with porous substances, undergoes partial decomposition with the formation of water and the liberation of chlorine.[1]

$$2HCl + O \rightleftarrows Cl_2 + H_2O + 14{,}700 \text{ cals.}$$

Under the stated conditions the yield is so small as to render the process impracticable unless a substance capable of acting as an oxygen carrier be employed. It was Deacon [2] who first evolved a successful chlorine manufacture using this reaction, and then by the employment as catalyst of pumice impregnated with a copper salt.

3. In the course of a series of investigations it was established by Hurter [3] (a collaborator of Deacon's) that the cheapest and most efficient catalyst available for the purpose was cupric chloride and, strangely

enough, this contact-material still holds the field against all others that have been proposed. His result was deduced from a diagram showing the affinity of all likely elements for oxygen, chlorine, and hydrogen —the diagram being obtained by plotting the heats of combination of these compounds against the atomic weight of the element concerned—from which it could be seen at a glance that no other metal than copper forms two oxides and two chlorides in which the combination is of so loose a character. The enquiry is mentioned here, since it furnishes one of the few cases in which the most useful catalyst has been selected, or at least the selection confirmed, from theoretical considerations.

4. During the early stages of the development of the Deacon process, the working results proved somewhat unsatisfactory. For some cause, then unexplained, the catalyst was quickly rendered inactive when "roaster gas" was employed, the latter, of course, containing as impurity the products of combustion from the open furnaces in which the second stage of the salt-cake process is effected.

The disadvantages attendant upon the use of "roaster gas" have been overcome largely as a result of the researches of Hasenclever.[4] This investigator attributed the rapid deterioration of the catalyst to the presence of sulphur trioxide in the gas, whereby a coating of sulphate was formed on the copper chloride employed; and proposed to eliminate this injurious effect by first absorbing the "roaster gas" in water, and then treating the resulting impure acid with hot sulphuric acid and air, by which means a mixture of pure gaseous hydrochloric acid with the requisite amount of air could be obtained.[5] Other remedies have been suggested, but Hasenclever's process is admittedly the most thorough.

As would be expected, sulphur trioxide is not the

only undesirable impurity in the technical gases. Oxide of arsenic produces arsenate of copper, which is even less reactive than the sulphate. Another impurity which exerts a deleterious influence is sulphur dioxide, for in the decomposer it is converted into sulphuric acid. Kolb [6] provides for the removal of both the dioxide and trioxide of sulphur by passing the "roaster gas" over lumps of salt, as in Hargreave's process described later. Both gases are absorbed, and by interaction with the salt generate a little more hydrochloric acid, which passes along with the unchanged hydrochloric acid of the furnace gases. According to Gaskell,[7] the removal of sulphuric and arsenic acids can be effected by adding to the contact mass such substances as have a greater affinity for the two impurities than copper has, e.g., calcium or magnesium chloride.

5. It is now recognised that cupric chloride is one of the most sensitive of catalysts to "poisonous" substances. On account of the small traces of impurities, such as the above-mentioned arsenic compounds, which it is impossible entirely to remove, as well as by reason of a gradual volatilisation of the copper salt, it is found necessary to renew the catalytic material at regular intervals.

This is effected in the most satisfactory manner by the type of decomposer [8] shown in Fig. 3, comprising an upright iron cylinder A, within which a cylindrical ring of contact material B is supported by iron shutters, C. The annular space between the shutters is divided into six compartments, each of which is emptied in succession every fortnight. The contact mass, wholly renewed in this way every three months, consists of broken brick which has been soaked in a solution of cupric chloride, and contains when dry from 0·6 to 0·7% metallic copper. Entering by the pipe D on the circumference of the cylinder, the gases from the salt-cake furnace pass through the contact

mass into the inner space and are led away by the pipe E.

6. The regulation of the temperature of the reaction in the decomposer is one of the primary considerations of the process. To obtain a good yield of chlorine the temperature must be kept as low as possible, seeing that the reaction is exothermic. But the lower the temperature falls, the less becomes the reaction velocity, notwithstanding the use of a catalyst. The two technical requirements of com-

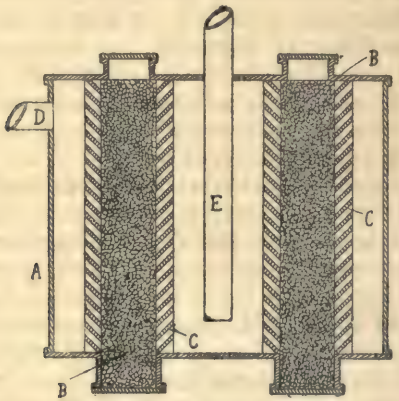

FIG. 3.

pleteness of reaction and highest possible velocity are therefore conflicting, and a compromise has to be effected by fixing what is known as an " optimum " temperature, or a temperature below which it is impracticable to go. The most suitable temperature appears to be at 450—460° ; above this volatilisation becomes excessive, whilst below it the yield is much diminished.

The rate of flow of the gases must be adjusted to allow them to attain equilibrium in the converter. Of course, the equilibrium does not depend altogether

upon this nor upon the temperature, but also upon the proportion of the constituents of the gases. Thus, the more air there is present, the more complete will be the equilibrium in favour of chlorine production. In practice, a mixture of 25% acid and 75% air is employed.

Under these conditions, nevertheless, only about two-thirds of the hydrochloric acid is converted into chlorine, and the undecomposed acid has therefore to be recovered, usually in a scrubbing arrangement. Even then, a much greater percentage of the acid is utilised than in any process employing either natural or recovered manganese dioxide.

7. The sensitiveness of cupric chloride has naturally induced investigators to seek other contact substances for the production of chlorine from gaseous hydrochloric acid. Among these are ferric chloride,[9] platinised asbestos,[10] a mixture of magnesium and manganese chlorides with magnesium sulphate,[11] the chlorides of the rare earths,[12] and the double compounds or mixtures of cupric chloride with other chlorides [13]; but the application of none of these materials, so far as is known, has emerged from the experimental stage. This list, although incomplete, will be sufficient to show how numerous and varied are the catalysts for the interaction under consideration.

8. The mechanism of the reaction is usually explained on the basis of an intermediate formation of an oxychloride of copper, $CuO \cdot CuCl_2$. The following then comprises the cycle of reactions :—

$$2CuCl_2 = Cu_2Cl_2 + Cl_2$$
$$Cu_2Cl_2 + O = Cl \cdot Cu \cdot O \cdot Cu \cdot Cl$$
$$Cu_2OCl_2 + 2HCl = H_2O + 2CuCl_2$$

II. Hargreaves-Robinson Process.

9. The direct process for the manufacture of salt-cake, first established on a successful practical scale

by Hargreaves and Robinson [14] in 1870, is deserving of mention in view of its later developments. Originally the process involved no catalyst, but consisted simply of the passage of pyrites gases over suitably-prepared common salt at 500—550° in a series of chambers, giving rise to the following reaction :—

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl.$$

10. In 1873 they proposed the addition of copper, manganese, or chromium, or their compounds [15]; and again in 1886 suggested increasing the speed of the reaction by the addition of a little ferric oxide to the salt.[16] Other substances have been put forward for the same purpose, but copper oxide and ferric oxide (particularly the former) appear to have the greatest influence.

To take advantage of the catalytic activity of the copper and iron oxides, the common salt is moistened prior to moulding with a solution of copper or iron sulphate or both, the added content varying between 0·1 and 1·0% in terms of metal.[17] The upper limit is only possible when the resulting salt-cake is intended for the Leblanc soda process, for there a little impurity has no effect; but where a purer material is required, for use for instance in glass works, only a very small amount of the catalyst may be added. The addition of these materials not only increases the velocity of the interaction, but also diminishes the temperature of decomposition. Most probably, the purpose of the added material is to promote the combination of the sulphur dioxide and oxygen to sulphuric anhydride, which then reacts with the common salt.

III. Claus-Chance Process.

11. At one time, the greatest source of inconvenience to the manufacturer of alkali by the Leblanc process was associated with the disposal of the "tank-

waste" or "alkali waste,"—the insoluble residue, containing some 40—60% calcium sulphide, which remains after lixiviation of "black ash"—on account both of the space it took up and the annoyance its smell occasioned to the neighbourhood surrounding the works.

Several attempts were made to work up this by-product, all of which proved unsuccessful until in 1887 the firm of Chance Bros.,[18] after the expenditure of much time and money, succeeded in devising a process for the recovery of most of the contained sulphur at a price permitting competition with Sicilian brimstone. Incidentally, the achievement was a fortunate one for the Leblanc process, since it has enabled it to compete with its younger and more vigorous rival, the Solvay ammonia-soda process. It is stated that from 30,000 to 40,000 tons of sulphur are annually recovered by this process in Great Britain alone.

12. The method is primarily based upon that patented in 1837 by Gossage [19] (who lost his fortune in futile endeavours to establish it on a commercial footing), which consists in decomposing the calcium sulphide of the "tank-waste" by lime-kiln gases, followed by the combustion of the sulphuretted hydrogen obtained. It is the latter part of the process that has catalytic interest, for it is accomplished according to a method devised by Claus,[20] in which the gas, after admixture with air in the combining proportions, is passed through a hot bed of solid material, such as oxide of iron, oxide of manganese, alumina, etc., in order to effect incomplete or fractional combustion according to the equation—

$$H_2S + 0 = H_2O + S + 55{,}000 \text{ cals.}$$

Of the substances tried as catalysts, however, none has been found to give such good results as hydrated ferric oxide.

13. In the usual construction of apparatus the Claus kiln, as it is called, comprises a cylinder provided internally with a grating upon which rests a layer of broken firebrick, with a further layer of bog-iron ore—a suitable form of hydrated oxide of iron—superimposed thereon. The combustible mixture, usually about four volumes of air to five volumes of 38% sulphuretted hydrogen, enters at the top and passes through the porous layers, where it is burnt to sulphur vapour and steam. The products are then drawn from the bottom into a series of condensing chambers, where part of the sulphur vapour condenses to liquid sulphur and the remainder as flowers of sulphur along with the uncondensed steam. The reaction in the kiln is far from complete, for from 15 to 20% of sulphur escapes from the condensing chambers in the form of sulphur dioxide and sulphuretted hydrogen. The former is removed by scrubbing with water and the latter by the passage of the waste gas through oxide of iron purifiers.

The temperature of the process is maintained by the heat of the reaction itself, and should not be allowed to fall below 200°. To start the reaction, a few shovelfuls of red-hot coal are thrown on to the oxide, and the temperature is then regulated by controlling the speed of the gas.

When once the necessary temperature has been reached, the reaction is found to proceed fairly satisfactorily with other contact material such as broken brick, but the working temperature then becomes higher than when ferric oxide only is employed. For starting the reaction, however, ferric oxide or similar contact material must be employed; hence the two layers in the Claus kiln. Recently it has been found that the temperature can be still further reduced by using dried "Weldon mud,"[21] the insoluble manganites of manganese and calcium, which are its principal constituents, serving as

excellent catalysts. Bauxite [22] is another material which is being used as a substitute for oxide of iron, and according to all reports based upon continued practical tests, it has proved an efficient catalyst for this purpose.

14. As mentioned when dealing with the Contact process for sulphuric acid, the catalytic activity of ferric oxide is to be attributed to the readiness of its transformation into some lower oxide when an oxidisable compound is present and its subsequent easy re-oxidation by atmospheric air.

REFERENCES FOR CHAPTER III.

[1] B. P., 10528/1845 (Oxland).
[2] B. P., 1403/1868.
[3] *J. Soc. Chem. Ind.*, 1883, *2*, 106.
[4] *Ber.*, 1876, *9*, 1070.
[5] B. P., 3393/1883.
[6] B. P., 6500/1891.
[7] B. P., 25024/1893.
[8] B. P., 11967/1894 (United Alkali Co.).
[9] B. P., 3080/1871 (Henderson).
[10] B. P., 2170/1871 (Weldon).
[11] B. P., 17272/1889 (de Wilde and Reychler).
[12] D. R. P., 150226 (Ditz and Margosches).
[13] D. R. P., 197955 (Dieffenbach).
[14] First B. P., 46/1870.
[15] B. P., 828/1873.
[16] B. P., 5682/1886.
[17] Fr. P., 384144/1907 (Hargreaves).
[18] B. P., 8666/1887.
[19] B. P., 7416/1837.
[20] B. Ps., 5958-9/1883.
[21] Carpenter and Linder, *J. Soc. Chem. Ind.*, 1903, *22*, 457.
[22] B. P., 3122/1906 (Chemische Fabrik Rhenania).

BIBLIOGRAPHY.

" Sulphuric Acid and Alkali," Vol. II. (1909) and Vol. III. (1911)—Lunge.
" The Alkali Industry "—Partington (1918).

CHAPTER IV.

Fixation of Atmospheric Nitrogen.

1. As long ago as 1898 Sir William Crookes[1] drew attention to the possibility of the early exhaustion of the nitrate deposits of Chile. The significance of this warning depended upon the fact that the only other source of inorganic nitrogen compounds available at that time, viz., the ammoniacal by-products obtained in the destructive distillation of coal, could never be anything like enough to meet the rapidly increasing demands of chemical industry and agriculture.

In looking around for some practical means for averting the prospect of an ultimate nitrogen starvation, chemists naturally turned to the inexhaustible store of free nitrogen which the atmosphere contains, for the most obvious solution to the problem would be to convert this nitrogen in some way or other into compounds of technical value. During the last twenty years the problem has been repeatedly attacked, mainly upon these lines; and as the result of a prodigious amount of research, quite a number of different methods for the fixation of atmospheric nitrogen have been worked out, and some of them established on a most extensive commercial scale. Since several of the processes are essentially catalytic in character, their investigation has contributed very appreciably to the sum total of our knowledge of catalysis.

2. The recent war has emphasised the importance of the new industries. From the first, Germany had

foreseen the value of nitrogen-fixation processes from the point of view of the manufacture of explosives, and their industrial development had been fostered. Indeed, Germany's decision to declare war appears to have been influenced not a little by the realisation of her growing independence of imported nitrate. The Allied Powers, on the other hand, have always relied to a heavy extent upon their imports of sea-borne nitrate, with the result that the nitrate situation during the war was one of the most important and critical that confronted their statesmen. It remains to be seen whether, if only in the interests of national security, Great Britain will insure herself against future contingencies of this kind by the establishment of nitrogen-fixation processes upon a considerable manufacturing scale.

As indicative of the enormous expansion that has arisen out of the war, it might be mentioned that whereas in 1914 the estimated capacity of nitrogen-fixation plant represented about 10% of the world's supplies of combined nitrogen, this has now grown to a total of 30%, and is likely to increase.

3. Reverting to the industrial processes, we find that three distinct methods are involved, viz. :—

(1) The direct oxidation of atmospheric nitrogen to its oxides by means of the electric arc, as in the processes of Birkeland and Eyde, Schönherr, and Pauling; or by the combustion of fuel products at high temperatures, as in the Häusser and Bender processes.

(2) The high-temperature fixation of nitrogen by metals or metallic compounds, which forms the basis of the Aluminium Nitride (Serpek) process, the Cyanamide (Frank and Caro) process, and the Cyanide (Bucher) process.

(3) The direct synthesis of ammonia, associated with the name of Haber.

In addition, the processes for the oxidation of ammonia should be mentioned, for they provide a means for converting the end-product of the processes referred to under (2) and (3) above into the commercially important nitric acid.

Of the above-mentioned, the processes which depend primarily upon catalytic phenomena are those for the synthesis of ammonia and for the oxidation of ammonia to nitric acid; but several of the others, which have some interest catalytically, will also come under consideration.

I. Ammonia-Synthesis Process.

4. The affinity of nitrogen for hydrogen, either at high temperatures or under the influence of spark or silent discharge, is so small as to be almost negligible. Even with the aid of a catalyst, the smallness of the yield was formerly considered to hold out no prospect of commercial advantage.

In 1904, Haber [2] undertook the investigation of the temperature equilibrium of ammonia, using modern physico-chemical methods. Nernst,[3] too, examined the equilibrium problem in 1907, but from the standpoint of the influence of pressure, using pressures as high as 70 atmospheres. Both investigators employed a catalyst to promote the attainment of equilibrium. From the figures communicated in each case, the practical synthesis of ammonia appeared almost a hopeless problem.

Undismayed by these unpromising results, Haber [4] allied himself with the chemists of the Badische Anilin und Soda Fabrik, and conducted further experiments in which almost unprecedentedly high pressures were employed. As the result of these experiments, they were finally able to show that ammonia is actually capable of synthesis on a technical scale, the essential factor for success being

the employment of pressures of from 150—250 atmospheres.[5]

Stupendous difficulties had to be contended with by Haber in connection with his investigation and by the chemists of the above-mentioned firm in its subsequent industrial development. By the manner in which all obstacles were surmounted,[6] the process ranks among the most brilliant achievements in the history of chemistry. As illustrative of the difficulties encountered, it might be mentioned that steel loses its carbon by the corrosive action of the gaseous mixture at elevated temperatures, and that iron becomes pervious to hydrogen under the high pressures involved. Furthermore, the presence of very small quantities of oxygen in the reacting gases renders them explosive, and necessitates the operation being carried out in bomb-proof shelters.

5. Of the actual construction of the apparatus very few details are forthcoming, despite the fact that the first factory of the above firm was completed in 1913, and that for the year 1917 it is estimated that no less than half a million tons of synthetic ammonium sulphate were produced. Owing to the secrecy observed, the commercial development of the process has so far been entirely confined to Germany. In this connection, though, it is satisfactory to learn that a factory for the manufacture of synthetic ammonia is in process of erection in England.

Some idea of the apparatus, nevertheless, may be gathered from a consideration of the diagrammatic sketch [7] shown in Fig. 4. A dried mixture of the gases, in the theoretical proportions of three volumes of hydrogen to one of nitrogen and under a compression of about 150 atmospheres, is passed through a heat-interchanger E consisting of a double coil, to the annular space between two tubes A and B, the

first of which contains the catalytic material, whilst the second is surrounded by an electric heating coil.

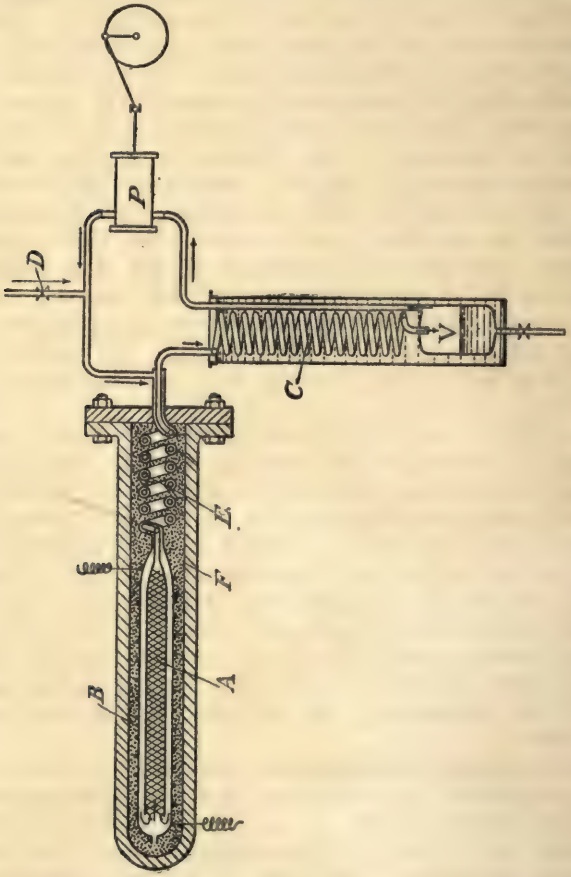

FIG. 4.

Both tubes are embedded in insulating packing contained in an outer tube F, so that the temperature can be maintained at any point between 500° and

700°. After passing through the catalysing material and the inner tube of the heat-interchanger, the gases reach a condenser C maintained at a temperature of $-75°$, where the liquid ammonia collects in a vessel V. The uncondensed gases are forced again through the circuit by means of a pump P, fresh nitrogen and hydrogen being introduced by the valved pipe D. The heat-interchanger is designed to transfer the heat evolved by the reaction in the catalyser to the cooled ingoing gases.

6. Returning now from this brief glance at the process, consideration must be given to the large amount of pioneer work which enabled Haber to define *à priori* all the conditions of the problem.

The union of nitrogen and hydrogen can be represented as follows :—

$$\underset{\text{(2 vols.)}}{N_2} + \underset{\text{(6 vols.)}}{3H_2} = \underset{\text{(4 vols.)}}{2NH_3} + 11{,}890 \text{ cals.}$$

From this equation, the following conclusions may be drawn (see Chapter I, sections 7 and 8) :—

(1) Since the combination is accompanied by a diminution of pressure at constant volume, increase of pressure will increase the concentration of ammonia at the equilibrium for a given temperature.

(2) The reaction being exothermic, an increase of temperature will diminish the concentration, assuming the pressure remains constant.

If there were no other considerations than these, it would follow that the pressure ought to be kept as high as possible and the temperature as low as possible.

In the following table are embodied some of Haber's results, showing the equilibrium concentrations of ammonia at various temperatures and pressures.

Pressure (in atmospheres).	Temperature °C.							
	200	300	400	500	600	700	800	900
1	15·3	2·18	0·44	0·13	0·05	0·02	0·01	·006
30	67·6	31·8	10·7	3·62	1·43	0·66	0·35	0·21
100	80·6	52·1	25·1	10·4	4·5	2·1	1·1	0·7
200	85·8	62·8	36·3	17·6	8·2	4·1	2·2	1·3

The figures will be found to bear out the conclusions already arrived at.

There still remain two factors, however, of which no account has yet been taken, viz., the rapid decrease in the reaction velocity with fall of temperature, and the accelerating influence of a catalyst upon the rate of attainment of equilibrium at any temperature. The net result is to fix a lower limit to the temperature consistent with the practicability of the process. As a matter of fact it is found that, using the best catalysts known, the velocity of the reaction becomes insufficient from the technical point of view at temperatures below 500°.

So far it has been assumed that the gases are allowed to remain in contact with the catalyst for at least such a time as will permit of the attainment of equilibrium. In the technical process, however, it is found necessary to pass the gases through the catalyser at a faster rate than this; for experiments have shown that, whilst the ammonia concentration necessarily decreases as the rate of flow increases, the product of the concentration and the rate of flow, which is a measure of the amount of ammonia produced in unit time, actually rises, and to no inconsiderable extent, until a certain maximum is reached. Thus, within limits, a premium is placed upon a rapid circulation.

Under no circumstances, it may be observed, are

the yields so high (they are of the order of 3—7%) as to render it remunerative to allow the residual gases to escape into the atmosphere after the reaction products have been removed, and it is for this reason that a continuous process has been adopted.

7. Recognising the importance that is attached to the catalytic function, the Badische firm has made a very minute investigation into the relative efficiencies of various materials and the effect of extraneous bodies upon their activity. The results in these directions are of first-rate importance.

The most favourable catalysts appear to be osmium [8] and uranium.[9] The former is ruled out of consideration for industrial application by reason of its rarity and costliness, whilst the latter suffers from the disability of being rapidly rendered inactive by traces of water or air in the reaction gases.

Judging by the most recent patents, pure iron [10] is the catalyst generally employed in this process. In the interests of efficiency, it is prepared from the oxide, which has been preliminarily purified by alternate reduction and oxidation, by a final reduction at a comparatively low temperature, preferably not exceeding 600°. Of the remaining substances which catalyse the reaction, and they are bewilderingly numerous, the most interesting are molybdenum [11] and molybdates, tungsten [12] and its alloys, and cerium [13] and its congeners. Platinum, on the other hand, though related to osmium, possesses but slight catalytic activity.

8. The most important feature attached to the investigation of the Badische firm was the discovery that the activity of the catalytic iron can be increased by the addition of certain foreign bodies.[14] These "promoters" (see Chapter I, section 16) include *inter alia* the oxides, hydroxides, and salts of the alkali, alkaline earth, and rare earth metals. For example, an iron-potash catalyst is particularly

active. As a general rule, compounds of those metals which yield non-reducible oxides and salts are suitable for use as promoters. All the catalysts appear to possess the capacity for invigoration by this means, requiring just a trace of the added body in order to develop a considerably enhanced activity.

9. Of course, contamination with certain substances has to be carefully avoided. As in the case of the contact reactions previously considered, there exist bodies which, even when present in the smallest traces, act as poisons to the catalyst. In the present instance, the great trouble occasioned by them necessitated a minute study of the influence of all possible impurities.[15] Examples of bodies acting deleteriously are to be found in sulphur, phosphorus, arsenic, and their compounds, as also such carbonaceous compounds as lubricating oil, and certain metals of low melting-point, which can readily be obtained by reduction from their compounds but are not themselves catalysts. Such minute quantities of any of the above-mentioned as are to be found almost always in the purest commercial products and so-called pure gases are sufficient to diminish very seriously the catalytic activity. In Chapter I, section 15, for instance, it is mentioned that an impurity of $\frac{1}{100}\%$ sulphur in the iron used for this process renders it nearly useless.

In view of these facts, every care is taken both to obtain pure contact material and to free the reacting gases from all poisonous bodies. The first is a comparatively easy matter, the ordinary methods of purification being employed. The removal of contact poisons from the reacting gases is a more difficult proceeding, particularly as economic considerations have brought about the replacement of the expensive electrolytic hydrogen formerly employed by the cheaper though less pure hydrogen obtained from coal by methods which will be referred to in Chapter V.

The nitrogen is most economically obtained by low-temperature separation from air. In general, the gases are filtered and washed, and then conducted over various solid absorption agents; whilst in some cases complete innocuousness is obtained by passage over a portion of the same material as is employed as catalyst before introduction into the catalyser.[13]

10. Two recent developments of the Badische process are deserving of mention. The difficulties which presented themselves in connection with the heating of the apparatus have now been overcome by injecting air into the gaseous mixture until the requisite temperature has been reached, and then so controlling the working conditions that the heat is maintained by the reaction energy. In this way the power requirements are reduced to a very low figure. Furthermore, instead of removing the ammonia by refrigeration, it is now absorbed by means of water under compression, effecting a more efficient removal thereby, though the gases require re-drying before being again introduced into the cycle.

11. Some modifications of the Badische process, differing mainly in the degree of pressure employed, are at present attracting attention. On the one hand there is the process of the General Chemical Company [16] of U.S.A., which aims at the reduction of the pressure to the neighbourhood of 100 atmospheres; whilst on the other there is the French process of Claude [17] in which the pressure is to be forced as high as 2,000 atmospheres or even higher. It remains to be seen, however, whether in the latter case present-day chemical engineering can cope with the employment of such enormous pressures. At present, a full-size commercial unit is being erected in France.

12. In considering the part which the catalyst plays in the synthesis of ammonia, it should be borne in mind that a good many of the catalysts are capable of forming both hydrides and nitrides. Whatever,

therefore, may be the physical influence of the fineness of division of the catalyst, at least some part of its activity must be assigned to the intermediate formation of nitride-hydride complexes. One might go still further and regard a promoter as a body which possesses the capacity for adjusting the ratio in which the nitrogen and hydrogen are temporarily combined with the catalyst to that required for the synthesis—a hypothesis which is supported by the fact that the promoters are in the main nitride-forming substances. A poison, on the other hand, may prevent access of the reacting gases to the catalyst by producing a film upon its surface.

II. Ammonia-Oxidation Process.

13. Though Kuhlmann [18] had observed in 1839 that ammonia could be oxidised to nitric acid in the presence of platinum, no commercial advantage was taken of the fact until 1909, when, after an elaborate investigation of the whole reaction by Ostwald, in which the practicability of the process was proved and tested, a large-scale plant was laid down in Germany. Considerable technical development of the process has since taken place, particularly during the war in the country of its origin, for Germany was compelled by the stoppage of her imports of nitrate to resort to ammonia as the source of nitric acid for war purposes.

14. The process depends upon the oxidation which ammonia undergoes when subjected to the action of heated air in the presence of certain catalysts, whereby nitric oxide is first produced according to the equation—

$$2NH_3 + 5O = 2NO + 3H_2O,$$

and this, by subsequent interaction with excess of oxygen, forms nitrous vapours which can be absorbed as nitric acid or nitrates.

In order to provide conditions which are more favourable to the incomplete oxidation of ammonia to oxides of nitrogen than to the formation of nitrogen by complete oxidation, the mixture of ammonia and air has to be circulated at high speeds over a catalyst, the most suitable of which appears to be platinum in the smooth solid form rather than in the finely-divided condition. This is the first desideratum.

The second is that, since the rate of oxidation with temperature rapidly increases to a maximum at about 750° and then falls off abruptly owing to decomposition of the ammonia into its constituents, the temperature conditions must be carefully controlled. In this connection, it might be noted that the reaction is a strongly exothermic one, so much so that the heat liberated by the reaction represented by the equation above, viz., 110,000 calories, is almost sufficient to maintain the catalyst at the reaction temperature under ordinary conditions. And lastly, by reason of the reversibility of the reaction, the oxygen should be kept in excess. This defines most of the conditions of the reaction.

15. In Ostwald's process [19] a mixture of ammonia and air is passed at a high speed through a tube of small cross-section containing a roll of corrugated platinum foil maintained at a temperature in the neighbourhood of 600°. The gaseous mixture found in practice to be most advantageous contains generally the proportions of one volume of ammonia to ten or more volumes of air. The length of the catalyst and the speed of circulation of the gases are so arranged as to give a time of contact not greater than $\frac{1}{100}$ second. After cooling, the gases are brought into contact with additional air to ensure complete oxidation of the nitric oxide to nitrogen dioxide and are then led into nitric acid absorption towers.

The difficulty of maintaining the contact temperature at anything like a constant value with high

gaseous speeds is overcome to some extent by heating the gases entering the catalytic chamber or the air alone at the expense of the hot products issuing therefrom. Under certain conditions of preheating and rate of flow, external heating of the catalyst may be dispensed with in view of the high exothermicity of the reaction. The only heating then necessary is that required for the initiation of the operation.

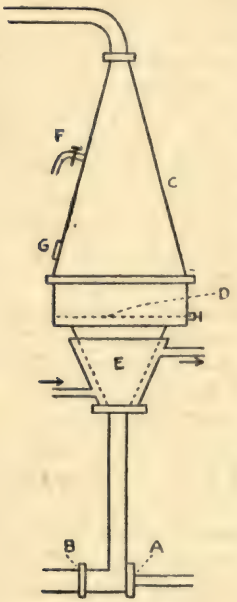

FIG. 5.

16. The use of a plug catalyst is now being replaced by that of a platinum screen or gauze, since it permits of larger size converters and is found to be more economical in the amount of platinum necessary per ton of nitric acid produced. Two or more gauzes, when placed in close proximity, are found to be decidedly advantageous; Kaiser,[20] for instance, employs four of these.

Again, to allow of increased rates of flow and a more complete control of the temperature of the catalyst, the platinum screen or screens are now being electrically heated. Such a modification makes for much greater simplicity, mainly by dispensing with the heat-interchanger formerly employed.

As an illustration of modern practice, the process of Frank and Caro,[21] which was extensively employed in Germany during the war, will be described. A diagram of the apparatus is shown in Fig. 5. The

pipes for ammonia and air are provided with gauge collars, A and B respectively, the diameters of which are so selected that the best mixture for oxidation is obtained. After the gases have been mixed by means of a revolving fan, they pass into a chamber C containing the electrically-heated platinum gauze D. The lower half of the chamber C is fitted with a cold-water jacket E, in order to prevent any decomposition of the ammonia by radiated heat before it reaches the catalyst; whilst the upper part of the catalytic chamber, besides being lined with aluminium to prevent any iron oxide from falling on to the catalyst, is provided with a sampling-cock F and a glass sight G for viewing the catalyst.

A converter of the multiple-gauze type capable of electrical heating has been designed by Partington [22] for use in making up the loss of nitrogen oxides in vitriol chambers (see Chapter II, section 3).

17. When platinum is employed as the catalyst—and, so far as is known, all the industrial plants at present in operation rely upon its use—the presence of certain compounds which poison it must be avoided. The presence of iron in the catalyst, for example, or of phosphine in the gases exerts a strong deleterious effect. The use, however, of ammonia from ammoniacal liquor or of cyanamide ammonia does not call for much purification, for the catalyst is not affected to any appreciable extent by such impurities as are likely to be present.

18. Other methods of ammonia oxidation have been proposed which are based upon the catalytic activity of certain base metals and their oxides, particularly when a promoter is present. Frank and Caro,[23] for instance, suggest the use of a mixture of ceria and thoria; Bayer & Co.[24] show that at 600—700° burnt pyrites (iron oxide containing some copper oxide) is a good catalyst; and the Badische Fabrik [25] claim that a mixture of oxides,

such as the oxide of a metal of the iron group with a small quantity of bismuth oxide, can replace the platinum ordinarily employed. Maxted [26] has recently investigated the relative efficiencies for various rates of flow of an iron catalyst which has been activated by admixture with such metals as copper, bismuth, cerium, and thorium, and his curves in this connection (see Fig. 6) are of considerable interest.

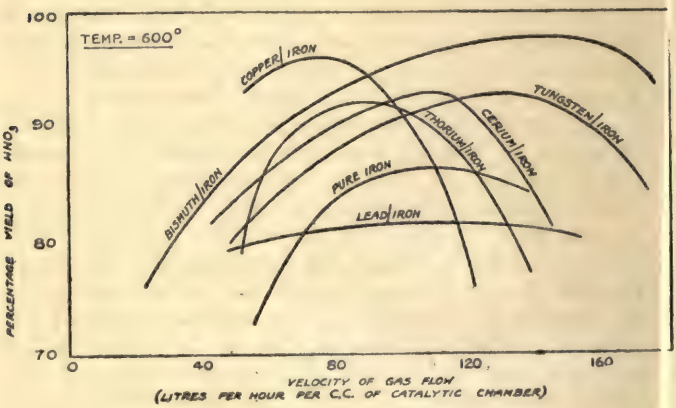

FIG. 6.

The diagram also brings out the relation between the yield and the gas flow, and indicates that for any particular catalyst a certain rate of flow should be adopted in order to obtain the most complete transformation. This does not necessarily mean that the conditions specified would be observed in actual practice, for economic considerations might make it advisable in this as in other cases to sacrifice high efficiency of conversion for greater output by the employment of still higher speeds.

In the case of these non-platinum catalysts, a

much longer period of contact with the reaction gases appears to be necessary. In addition, the amount of catalyst required detracts somewhat from the value of the method, not because of the cost, but on account of the difficulties which are introduced as regards uniformity of gas flow and of reaction temperature. There is always the danger, too, of the sintering of the powdered catalyst at the high temperatures required, resulting in impermeability after short use.

19. With all these ammonia-oxidation methods the energy requirements are low, rendering the process a very economical one. Since the same may be said of the ammonia-synthesis method, it might be predicted with a fair amount of assurance that a combination of the two processes will eventually render all other nitrogen-fixation processes obsolete, except perhaps in countries where water-power is abundant.

20. Before leaving the subject of nitrogen-fixation a glance must be given at one or two of the processes mentioned in section 3, which have interest catalytically.

III. Cyanamide Process.

21. Under certain conditions calcium carbide will combine with nitrogen to produce a complex nitrogenous body known as calcium cyanamide.

$$CaC_2 + N_2 = CaCN_2 + C.$$

This reaction is of great value technically, for it forms the basis of a process which has been worked on a large scale in several countries for some years. Germany alone is stated to have a productive capacity of 600,000 tons per annum.

Pure calcium carbide was shown by Moissan [27] to be quite indifferent to nitrogen at 1,200° ; yet

commercial carbide will absorb nitrogen with avidity at this temperature, as was shown by Frank and Caro,[28] the originators of the process. The difference in behaviour is to be attributed to the presence in commercial carbide of a small percentage of lime. Other substances exhibit a similar accelerating effect. The most useful of these appears to be calcium chloride, a 10% addition of which lowers the reaction temperature to such an extent that rapid azotisation takes place at temperatures of from 700° upwards.[29]

It should be observed, nevertheless, that the amounts of added material are so large comparatively as to cast doubt upon any explanation of the process on a catalytic basis only.

IV. Aluminium Nitride Process.

22. In its latest form, Serpek's process [30] consists simply of heating a mixture of bauxite and carbon in a current of nitrogen under pressure to a temperature of about 1,550° in a specially-designed electric furnace. The interaction takes the following course :—

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO.$$

Now, alumina, when pure—say, as pure as the final product of the process—reacts only very slightly with carbon, so that the presence of a trace of a foreign body appears to be essential to the production of the nitride. That is why bauxite is to be preferred as the starting material, because the impurities it contains, which are chiefly of a ferruginous nature, promote the interaction. Serpek [31] adds a trace of a metal, such as iron or copper ; the Badische firm [32] employ one of the oxides of certain elements, e.g., silicon or titanium, which can themselves form stable nitrides. On the whole, iron and silica exhibit the most active catalytic effect. Incidentally, it

might be mentioned that ferro-aluminium is now being used as the starting material, in which case the addition of a little calcium carbide is found to be beneficial.[33]

The reaction represented by the equation above is accelerated, too, by the presence of hydrogen in the nitrogen.[34] By combining the use of bauxite with the introduction of hydrogen into the gas, a more than cumulative effect results.[35] The reaction can then be rendered practicable at 1,250° or thereabouts, provided a large excess of nitrogen be used.

Unfortunately, there are one or two difficulties connected with this process which so far have militated against its successful commercial development.

V. Cyanide Process.

23. The last process to be considered is one which possesses considerable promise, and which bids fair, if the mechanical difficulties can be overcome, to develop into a serious rival to the established synthetic ammonia and cyanamide methods of nitrogen fixation.

A mixture of soda-ash and carbon in any form is heated in contact with a small quantity of finely-divided iron to a temperature of about 950°, whilst a stream of nitrogen or air is passed through it. The part played by the iron is undoubtedly that of a catalyst, for otherwise the interaction, which proceeds according to the following equation, requires much higher temperatures for a smaller conversion.

$$Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO - 138{,}500 \text{ cals.}$$

The resulting sodium cyanide is easily separated, either by distillation or lixiviation, and from this, by treatment with boiling alkali or steam, ammonia is produced.

It should be noted that, though the reaction as

represented above is strongly endothermic, the combustion of the three molecules of carbon monoxide to carbon dioxide can be made to yield 200,000 calories, so that the total process is an exothermic one.

The reaction is by no means new, and many attempts had previously been made to establish it on a works basis. Their failure is attributed by Bucher,[36] to whom much of the recent investigation of the method is due, to the omission of iron, which appears to be the only suitable technical catalyst when alkali carbonates are employed. The process is said to be a very advantageous one from the point of view of simplicity of plant, low energy requirements, and the capacity for employing nitrogen-containing gases instead of pure nitrogen.

REFERENCES FOR CHAPTER IV.

[1] Brit. Ass. Rep., 1898; see also his book "The Wheat Problem" (1917).
[2] *Zeitsch. anorg. Chem.*, 1905, *43*, 111; *44*, 341.
[3] *Zeitsch. Elektrochem.*, 1907, *13*, 521.
[4] See *Zeitsch. Elektrochem.*, 1910, *16*, 244.
[5] B. P.s, 17951/1909 (Badische), 14023/1910 (Haber).
[6] See Bernthsen, Eighth Int. Con. App. Chem., 1912, Vol. 28.
[7] B. P., 17951/1909 (Badische).
[8] B. P., 17642/1909 (Badische).
[9] B. P., 10441/1910 (Badische).
[10] B. P. 24657/1911 (Badische).
[11] B. P., 61/1911 (Badische).
[12] B. P., 1161/1912 (Badische).
[13] B. P., 5835/1911 (Badische).
[14] B. Ps., 19249/1910, 5833/1911, 5835/1911.
[15] B. Ps., 19249/1910 (Badische), 5835/1911 (Badische).
[16] B. P., 120546.
[17] First B. P., 130086.
[18] *Annalen*, 1839, *29*, 281.
[19] B. P.s, 698/1902, 8300/1902.
[20] B. P., 24035/1911.
[21] *Chem. Met. Eng.*, 1916, *14*, 425.
[22] *J. Soc. Chem. Ind.*, 1918, *37*, 337 R.
[23] D. R. P., 224329.
[24] B. P., 18594/1903.
[25] B. P., 13848/1914.

[26] *J. Soc. Chem. Ind.*, 1917, *36*, 777.
[27] *Compt. rend.*, 1894, *118*, 501.
[28] First B. P., 15066/1895.
[29] Bredig, *Zeitsch. Elektrochem.*, 1907, *13*, 69, 605.
[30] B. P., 13086/1910.
[31] B. P., 7507/1909.
[32] B. P., 16368/1910.
[33] B. P., 4287/1915 (Société Générale des Nitrures).
[34] B. P., 8348/1912 (Société Générale des Nitrures).
[35] B. P., 8349/1912 (Société Générale des Nitrures).
[36] *J. Ind. Eng. Chem.*, 1917, *9*, 233 ; see first B. P., 27713/1912.

BIBLIOGRAPHY.

" Fixation of Atmospheric Nitrogen "—Knox (1914).
" Utilisation of Atmospheric Nitrogen "—Norton (1912).
" Final Report of the Nitrogen Products Committee "—Cmd. 482 (1920).
Creighton—*J. Franklin Inst.*, 1919, *187*, 379, 599, 705 (contains a full bibliography).

CHAPTER V.

Surface Combustion, Incandescent Gas Mantles, Hydrogen Manufacture, Coal Gas Purification.

I. Surface Combustion.

1. Every student of chemistry is acquainted with the fact that a warm platinum wire, suspended in a non-explosive mixture of coal-gas and air, continues to glow until all the oxygen has disappeared. Davy [1] discovered this in 1817. A little later, Dulong and Thénard [2] showed that all solids—and not only the members of the platinum group, as Davy thought—possess the power of promoting combustion at temperatures below the ignition-point, the influence varying with the specific character and the fineness of division of the solid concerned. This and related discoveries were of prime importance ; yet until recently their only practical application has been the well-known Döbereiner lamp, or in its modern modification, the automatic gas-lighter.

2. The problem of " surface combustion," as the phenomenon has come to be called, has been fully investigated of late years by Bone and his collaborators. As the result of their researches, which date from 1902, the following facts have now been established :—

(1) All incandescent surfaces are capable of accelerating gaseous combustion; and very probably to an equal degree, for the differences between the catalytic powers of various surfaces gradually diminish as the temperature rises, until at incandescence they practically disappear.

It might be noticed, in passing, that this latter conclusion is borne out by Knietsch's experiments, referred to in Chapter II, section 8. Thus, from Fig. 1 it will be seen that at 850° there is little difference between the catalytic powers of platinum, pyrites cinders, or broken porcelain in sulphuric anhydride formation.

(2) The combustion takes place heterogeneously, that is to say, only in layers immediately in contact with the incandescent surface, and not homogeneously, or equally throughout the system.

(3) The catalytic process depends primarily upon condensation or absorption of one or other, or possibly both, of the reacting gases by the surface, whereby the gases are rendered "active," probably by ionisation.

(4) The incandescent surface becomes strongly negatively electrified during the combustion.

3. The first of these observations is utilised in the "Surface Combustion" process now to be described.

In this process, an explosive mixture of a combustible gas and air is brought into contact with a refractory solid placed in proximity to the body to be heated. The mixture should be in the proportions for complete combustion, or with air in slight excess, and must necessarily be injected on to, or forced through, the solid at a velocity greater than the speed of ignition of the mixture. On now igniting the issuing gases, the surface of the solid rapidly becomes incandescent, and the mixture continues to burn there without the formation of flame, but with the development of a large amount of radiant heat.

To make clear the *modus operandi*, two forms of apparatus, corresponding to the two fundamental types, will be described.

4. The first, shown diagrammatically in Fig. 7 and known as the "Diaphragm" adaptation,[3] com-

prises a diaphragm A of porous refractory material, through which the gaseous combustible mixture is forced under slight pressure from the chamber B. Soon after ignition of the gases on the exit face, the surface layer attains incandescence, and, by suitably adjusting the quantity of entering gases, the incandescence can be maintained there without any unburnt gases escaping whatsoever. This form finds application for domestic heating,[4] and also for the concentration and evaporation of solutions, in which latter case the apparatus is inverted over the concentrating pan.

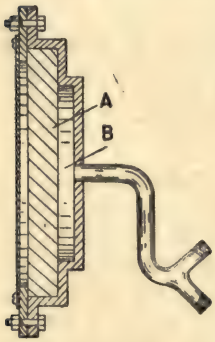

FIG. 7.

The degree of porosity is sufficient in all cases to relegate the question of back-firing beyond the need for consideration. The fineness or coarseness is determined, of course, by the quality and pressure of the combustible mixture employed. Temperatures of 800—900° (using coal gas) can readily be obtained by this means.

5. In the second and more important form of the apparatus, known as the "Granular Bed,"[5] the diaphragm is replaced by a number of refractory granules, and it is then on the surface of each of the granules that incandescence occurs, making the whole bed a white-hot mass. In Fig. 8 is shown a muffle furnace C surrounded by lumps of refractory material D, to which the combustible mixture in combining proportions is supplied by the pipe E, at a velocity in excess of the speed of inflammation of the mixture. By this means, high temperatures are easily attained. The maximum naturally depends upon the working

conditions, but in such a furnace as just described, temperatures in the neighbourhood of 1,400° or 1,500° become available.

The choice of refractory material is determined by the temperatures demanded. In the ordinary course a number of substances are at one's disposal, viz., calcined fireclay, ganister, etc. ; but when very high temperatures are in question, the choice is

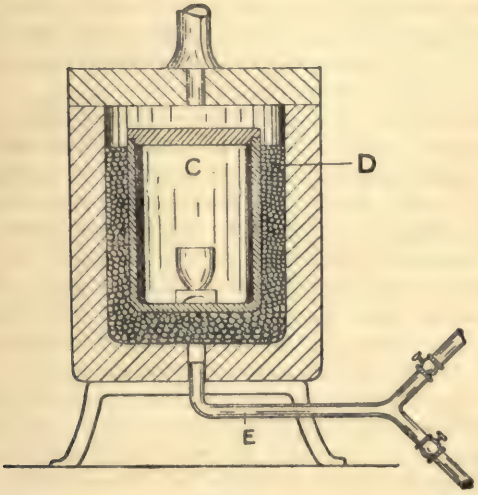

FIG. 8.

limited to the use of either calcined magnesia or carborundum.

The second method has been utilised in a number of industrial applications. For instance, the refractory material may function as a hearth or furnace,[6] or it may be packed into tubes which are immersed in water for steam-raising purposes (multitubular boiler),[7] or in metals or alloys which it is required to melt.[8]

6. The advantages of the process are manifold. In the first place, it is adapted for the employment of a large variety of combustible gases—blast-furnace gas, producer gas, water gas, coke-oven gas, coal gas, etc. Or, instead of using a combustible gas, a suitable mixture of atomised liquid fuel and air may be employed.[9] Furthermore, the process appears to be remarkable for its efficiency; in the case of tests with a gas-fired multitubular boiler, for instance, efficiencies of from 90 to 95 % have been recorded. The process is one of great flexibility, too, since the temperature can be almost instantly varied by altering the rate of feed of the gaseous mixture.

Incidentally, it might be mentioned that present-day power production is inclining more and more towards the substitution of gaseous or vapour fuel for the solid variety. There is also a tendency towards the extraction of a greater proportion of the by-products of coal distillation than before by a low-temperature carbonisation of the raw coal. And as this means that the gases obtained will be of low grade, the importance of a process like the present which can use such gases becomes apparent.

7. With regard to the mechanism of the process, the fundamental fact that the surface acts as a catalyst cannot be gainsaid, nor yet the general manner in which the surface acts. In the course of the Faraday-de la Rive controversy (1834—5), the rival theories were fiercely debated, de la Rive maintaining that surface combustion consists essentially of a series of rapidly alternating oxidations and reductions of the catalyst, whilst Faraday strongly upheld the view that the function of the solid is to condense the reacting gases upon the surface, thereby producing in the surface layer a condition comparable with that of high pressure. Bone's results amply prove the correctness of Faraday's physical explanation.

Attempts to probe deeper than this have not yet resulted in anything very definite. It is known, nevertheless, that incandescent surfaces emit streams of electrons travelling at high velocities: and the action of hot surfaces in promoting combustion may ultimately be found to depend upon the formation of layers of electrified gas, in which the chemical changes proceed with extraordinarily high velocity under the influence of the corpuscular discharge. Excellent support for this view is found in the fact already mentioned that the catalyst becomes negatively charged during the combustion process.

II. Incandescent Gas Mantles.

8. From the standpoint of surface catalysis, the subject of gas mantles possesses at least one feature of sufficient interest to make it worthy of mention here.

Soon after Welsbach [10] began his epoch-making investigations upon the luminous properties of the rare-earth oxides, he came to the conclusion that, of them all, thoria [11] appears to be the most satisfactory as an emitter of light. But he also made the curious observation that the more the thoria was purified, the less the light obtained from it. Attempts to account for this led, in 1892, to the discovery of the power exercised by a trace of ceria in augmenting the emissivity of thoria,[12] and to the consequent adoption as a basis for the gas mantle associated with his name of a mixture of 99% thoria and 1% ceria—a mixture which numerous later attempts have failed to improve upon, though other oxygen carriers such as chromium oxide [13] have been proposed.

The added component is known as an " excitant." Pure thoria gives a relatively poor light, but the continuous addition of ceria gradually increases the

luminosity to a maximum of tenfold when 1% is present, any further addition then diminishing the luminosity until, with 10%, the difference in effect is inappreciable. In present-day manufacture, the web of ramie fibre or artificial silk is impregnated with a 25—33% aqueous solution of thorium and cerium nitrates in the proportion of 99 : 1, to which a little hardening medium, usually beryllium nitrate, has been added.

9. The beneficial action of the ceria can be ascribed pretty definitely to its catalytic function in promoting the combustion of coal gas. As for the reason for its assistance, the power which many catalysts possess of existing in two or more states of oxidation applies to cerium, and the activity of ceria may perhaps be attributed to this.

III. Hydrogen Manufacture.

10. Hydrogen is now in such demand, especially for the hydrogenation of oils and the synthesis of ammonia, that the problem of its industrial preparation has attracted a very considerable amount of investigation.

11. Of the many methods which have been suggested, at least four have assumed commercial importance, viz. :—

(1) The electrolysis of water or some suitable electrolyte.
(2) The liquefaction of water gas and the separation of hydrogen from its constituents by fractionation (Linde-Frank-Caro process).
(3) The interaction of water gas and steam in the presence of a catalyst (Badische process).
(4) The alternate action of steam and water gas upon iron (Messerschmidt process).

12. As regards the above processes, only the third is catalytic. It is based upon the well-known

fact that water and carbon monoxide will interact at elevated temperatures and in the presence of a catalyst to produce hydrogen and carbon dioxide, according to the equation :—

$$H_2O + CO \rightleftarrows H_2 + CO_2 + 9{,}000 \text{ cals.}$$

As is indicated, the reaction is both reversible and exothermic, from which it follows that it is desirable both to keep the temperature low and to use a large excess of steam. So far as the evolution of heat is concerned, however, it is not found to be quite enough to maintain the gases at the reaction temperature and to cover the normal heat losses in the apparatus.

13. The Badische firm have carefully investigated the reaction with a view to the preparation of pure hydrogen from industrial gases, such as water gas or coke-oven gas, which contain a large proportion of carbon monoxide. Iron [14] or its oxide [15] was found to be the most advantageous catalyst, though other metals of the iron group [16] are stated to possess similar, if less marked, properties. Moreover, the activity of the catalyst could be enhanced to a very considerable extent by the addition of a promoter,[17] such as the oxygen compounds of chromium, thorium, uranium, beryllium, or antimony. Metallic couples,[18] particularly an iron-copper couple, have recently been suggested as catalysts in this connection.

The contact bodies just mentioned are not at all sensitive to impurities in the gases, provided, of course, that the amount be small, and it is only in some cases that the presence of sulphur, chlorine, phosphorus, or arsenic compounds has to be excluded. Crude water gas may therefore be employed, the only preliminary purification necessary being the removal of flue dust.

14. In carrying the reaction into practice—and the Badische firm manufacture the hydrogen for

their synthetic ammonia process in this way—a mixture of water gas containing excess of steam is passed at atmospheric pressure through a mass of iron oxide activated by the presence of chromium and thorium oxides, maintained at a temperature of 400—600°. External heating is quite unnecessary if a heat-interchanger be employed and oxygen or air be injected into the mixture,[19] for the heat of combustion of this oxygen with a part of the hydrogen present then provides the additional heat necessary for carrying on the process continuously. The carbon dioxide produced is removed in any convenient manner—for example, by compression on to water. The traces of carbon monoxide which contaminate the resulting hydrogen are found to have an injurious effect upon catalytic processes, and they have therefore to be eliminated either by interaction with calcium carbide, or with alkalies at elevated temperatures, or by passage through ammoniacal cuprous chloride.

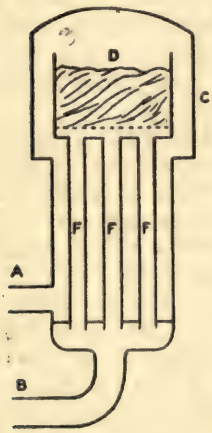

FIG. 9.

15. As the apparatus is of a type very useful in gaseous catalytic processes, a diagrammatic representation of it is shown in Fig. 9, from which it will be seen to comprise a converter or generator, which is so arranged as to combine the functions of catalysing chamber and heat-interchanger or regenerator. The mixture of water gas, steam and air in the requisite proportions enters the generator C by the pipe A, and before reaching the catalytic material D is heated by contact with the tubes F through which the hot

products of the reaction are flowing. After the reaction has been effected, the hot products flow back through the pipes F, parting thereby with their heat to the incoming gases, and issue from the generator by the pipe B. The temperature of the catalytic material is controlled by regulating the speed of the ingoing gases.

16. There are still one or two methods for hydrogen production which merit attention, for though they are not absolutely dependent upon the use of catalysts, the operation in each case is facilitated by their presence.

In one,[20] which invokes the aid of a catalyst to assist in the ordinary decomposition of hydrocarbons into their elements by heat, a mixture of hydrocarbon and steam is passed over a catalyst, such as nickel or its oxide suitably supported, at a temperature of 800—1,000°. On freeing the resulting gaseous mixture from carbon monoxide and dioxide, substantially pure hydrogen is obtained.

Another, known as the Bergius process, depends upon the behaviour of water when in contact with iron at a pressure sufficient to keep the water in the liquid state at a temperature above the boiling-point, say at 200—300.° Under these conditions, the water functions as an acid; its oxygen combines with the iron, leaving hydrogen in the pure state and at a sufficiently high pressure (up to 300 atmospheres) to permit of the gas being directly filled into cylinders without previous compression. The reaction is accelerated by the presence of certain salts,[21] such as sodium chloride and ferrous chloride, or of a metal, such as copper. If the iron be replaced by carbon,[22] the resulting hydrogen is mixed with carbon dioxide, which requires to be removed. Thallium chloride is stated to act catalytically in this case.

IV. Purification of Coal Gas.

17. *Elimination of Sulphuretted Hydrogen.*—The removal of the injurious hydrogen sulphide from coal gas, which the law demands, is generally effected by passing the gas through moistened absorbent materials, chief among which are lime, ferric oxide, and manganese dioxide. Sulphides are produced, which, in the case of the two latter materials, regenerate the original substance on exposure to the air, thereby permitting of repeated use of these absorbents. Such a process cannot, of course, be regarded as catalytic (see Chapter I, section 22).

In a development, however, the iron and manganese oxides are made to function catalytically. This is brought about by admitting a sufficient quantity of air into the gas to be purified to revivify the spent oxide *in situ* [23] and has the advantage of enabling the purifiers to be worked much longer without recharging. The process, in fact, is then the same as that in the Claus kiln, described in Chapter III, except, of course, for the temperature conditions, which must be so regulated as to prevent the formation of any sulphur dioxide.

18. *Elimination of Carbon Bisulphide.*—The sulphur compounds remaining in coal gas after the withdrawal of sulphuretted hydrogen consist mainly of carbon bisulphide. One of the processes for its removal—the Carpenter-Evans process [24]—consists in heating the gas to 430° and then passing it through chambers containing fireclay balls impregnated with nickel reduced from the chloride. The carbon bisulphide reacts with the hydrogen of the coal gas to produce sulphuretted hydrogen,

$$CS_2 + 2H_2 = 2H_2S + C,$$

which is removed from the gas, after its temperature has been reduced to that of the atmosphere, by

passage through iron oxide in the usual manner. The catalyst can be regenerated at monthly intervals by passing air through the chamber in order to burn out the carbon deposited upon the balls.

Although sulphuretted hydrogen is produced by the reaction it is essential to remove this impurity from the gas before treatment to prevent deterioration of the catalyst. Incidentally, the absence of any poisoning effect from the carbon bisulphide itself is rather a remarkable feature.

REFERENCES FOR CHAPTER V.

[1] *Phil. Trans.*, 1817, *107*, 77.
[2] *Ann. Chim. Phys.*, 1823, *23*, 440; *24*, 380.
[3] B. P., 25808/1909 (Bone).
[4] B. P., 10150/1910 (Bone).
[5] B. P., 29430/1909 (Bone).
[6] B. P., 5936/1912 (Bone).
[7] B. P., 4362/1910 (Bone).
[8] B. P., 625/1911 (Bone).
[9] B. P., 28477/1912 (Bonecourt Surface Combustion, Ltd.).
[10] See *Chem. News*, 1902, *85*, 254.
[11] B. P., 3592/1886.
[12] B. P., 124/1893.
[13] B. P., 25359/1899 (Sunlight Incandescent Co.).
[14] B. P., 26770/1912 (Badische).
[15] B. P., 27955/1912 (Badische).
[16] B. P., 8864/1913 (Badische).
[17] B. P., 27963/1913 (Badische).
[18] B. P., 6477/1914 (Buchanan and Maxted).
[19] B. P., 27117/1912 (Badische).
[20] B. P., 12978/1913 (Badische).
[21] B. P., 19002/1912 (Bergius).
[22] D. R. P., 259030 (Bergius).
[23] See, e.g., 17888/1899 (Chollar).
[24] Evans, *J. Soc. Chem. Ind.*, 1915, *34*, 9; Carpenter, *J. Gas Lighting*, 1914, *126*, 928.

BIBLIOGRAPHY.

SURFACE COMBUSTION :—
"Coal and its Scientific Uses" (Chapter XXII)—Bone (1918).
Bone—*J. Roy. Soc. Arts*, 1914, *62*, 787, 801, 818.

INCANDESCENT GAS MANTLES :—
"Das Gasglühlicht"—Böhm (1905) (contains a bibliography).
HYDROGEN :—
"Hydrogenation of Oils" (Chapters XIX to XXVII)—Ellis (1919).
"Chemistry and Manufacture of Hydrogen"—Teed (1919).

CHAPTER VI.

Hydrogenation.

1. The reduction of organic compounds by the old stock methods was always a tedious process. It is possible, however, to effect reduction in a simple straightforward manner by a method known as hydrogenation, i.e., by direct treatment with hydrogen of the substance to be reduced.

The inception of this method is to be attributed to the researches of Sabatier and his collaborators, beginning in 1897, upon the capacity of certain metals when in the finely-divided state for inducing a remarkable "activation" of hydrogen. By the aid of a metallic catalyst of this sort, they found that the union of unsaturated compounds with gaseous hydrogen or the direct replacement of an element in a saturated compound with hydrogen could readily be effected in a manner which permits of great regulation and adaptation. The method has been employed by Sabatier and his co-workers, Senderens, Mailhe, and others, for the preparation of a whole host of substances hitherto either unknown or else very difficult to obtain by other means; and in several instances the laboratory process has been promoted to the industrial stage with conspicuous success.

In Sabatier's method the substance to be hydrogenated is invariably treated when in the vaporous state; but other methods—associated with the names of Paal, Skita, Willstätter, and Ipatiew—have since been introduced in which the same prin-

ciple is applied to the treatment of liquid material. In the following pages, each of these methods will be considered.

(1) Catalytic Hydrogenation in the Vapour State.

2. The principle of Sabatier's method [1] is a simple one. The vapour of the substance to be reduced is mixed with hydrogen and passed over specific metallic catalysts maintained at temperatures situated usually between 150° and 200°. Complete hydrogenation takes place during the short time that the mixture is passing over the catalyst. Rapidity, however, is not the only advantage, for the method furnishes excellent yields with the minimum of attention.

3. The metals which are suitable as catalysts are nickel, cobalt, platinum, iron, and copper, of which nickel is far and away the most active, the others being arranged in the order of diminishing activity. As would be expected, the practicability of the method depends largely upon the condition in which the metal is used. It must be prepared by reduction of the oxide at a pre-determined temperature, and preferably in the same vessel in which the subsequent hydrogenation is to take place. Reduction at a low temperature is found to yield a catalyst which is too active and too sensitive to external influences, whereas reduction at a high temperature reduces the catalytic power almost to zero. Consequently a suitable intermediate temperature must be chosen. Sabatier finds that the best nickel for the purpose is produced by dissolving the metal in nitric acid, calcining the nitrate at a dull red heat, and then reducing the oxide slowly at a temperature of about 300—325°, until water is no longer given off. After the nickel has been prepared as described,

it is necessary to keep it out of contact with the air, for it is extremely pyrophoric and quickly loses its activity on exposure.

4. As in the case of the catalysts previously considered, the activity is much enhanced by the addition of promoters.[2] The Badische firm, to whom the merit of the discovery must be ascribed, employ in particular in this connection the oxide or an oxygen salt of an earth metal, or of beryllium, magnesium, manganese, uranium, vanadium, etc., as well as the phosphates, molybdates, and tungstates of the alkaline earths.

Weight for weight, too, the efficiency of pure nickel is not so great as that which has had its active surface increased by the aid of some suitable supporting material such as pumice, kieselguhr, or charcoal.

5. There are two conditions for the conductance of the process, the rigorous observance of which is indispensable to success. In the first place, the materials used, whether hydrogen, metal or organic compound, must be as pure as can be obtained, since any impurity is readily absorbed by the catalyst to the detriment of its activity. Sulphur and its volatile compounds, as well as the halogens, are particularly to be avoided in this respect, as also, though to a lesser degree, arsenic and phosphorus with their volatile compounds. Electrolytic hydrogen, or hydrogen of equivalent purity, appears to be essential. Even then the catalyst must succumb sooner or later to the toxic effects of minute impurities impossible to remove, and in consequence, the desirability of frequent renewal needs emphasis.

Furthermore, it must be clearly recognised that a particular hydrogenation will only take place within pre-determined limits of temperature, and that any excursion outside of these limits must necessarily result in the contamination of the final product with

undesired subsidiary products. The more difficult the reduction, the narrower is the range of temperature, and *vice versâ*. The reduction of ethylene bonds, for instance, being easily effected, is possible within a comparatively wide temperature interval; whereas aromatic rings in general require careful temperature adjustment.

6. In its elementary aspect, the apparatus employed by Sabatier is shown in Fig. 10. The industrial modifications, of course, vary with the nature of the process, but the principle of the arrange-

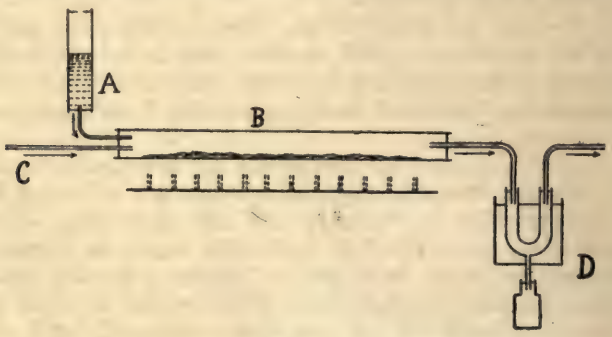

FIG. 10.

ment will be evident from a consideration of this laboratory apparatus. The tube B containing the reduced metal is heated in a furnace or oil-bath or preferably by an electrical resistance,[3] the latter being employed where uniformity of temperature is essential. Pure hydrogen is introduced at C, and sweeps in some of the organic compound, conveniently represented as liquid and passing in from A; if the compound be solid, it is melted in a distilling bulb and the hydrogen bubbled through. Contact with the reduced metal, usually nickel, effects the reduction, and the products are condensed in D. In every case, it should be noted, the substance under

treatment, as also the transformation product, must be kept in the state of vapour.

7. Having thus briefly outlined the method and the conditions essential to success, attention will now be directed to some of the important results obtained by its aid. A cursory glance only can be attempted here, for it must be remembered that, whereas but a few examples can be instanced, in reality they are legion.

8. To begin with, fatty and aromatic nitro-bodies are found to yield the corresponding amine. A practical example of this is the manufacture of aniline,[4] for by this method the reduction of nitro-benzene can be easily realised in a continuous way. Copper, however, is preferable to nickel as the catalyst, because it never brings about the further hydrogenation of the aniline produced. Moreover, copper not being so sensitive as nickel to disturbing factors, water gas or even purified coal gas may be substituted for pure hydrogen. The activity of the copper may be promoted by the addition of alkaline compounds or metallic oxides.[5] It might be mentioned in this connection that in the ordinary process for the manufacture of aniline by the reduction of nitro-benzene, using iron and hydrochloric or acetic acid, the iron functions in the manner of a catalyst, for only 5% of the acid theoretically necessary is really employed.

Again, ketones of both series are readily hydrogenated. Acetone, for instance, is converted into isopropyl alcohol with an efficiency which compares very favourably with that which results from the use of sodium amalgam.

Aldehydes can be made to yield the corresponding alcohol. Of practical value in this connection is the production of ethyl alcohol by the hydrogenation of acetaldehyde, a reaction which is dealt with in greater detail in Chapter VIII, section 12.

An interesting case is that of the monoxide and

dioxide of carbon. From the former, formaldehyde and the commercially important methyl alcohol might be expected, whereas in both cases only methane is produced. This reaction has been utilised to advantage in a process [6] which aims at increasing the calorific value of water gas by eliminating the carbon monoxide constituent, and consists in passing the gas over reduced nickel at 350—400°. By means of this reaction the residual coke of gas-works may ultimately be utilised for the manufacture of lighting gas.[7] By working under pressure and employing gaseous mixtures of carbon monoxide and hydrogen in which the percentage of hydrogen is comparatively small, liquid hydrocarbons both saturated and unsaturated are stated to be produced, together with a certain amount of alcohols, ketones, and acids.[8]

9. The above reactions involve the substitution of hydrogen for oxygen in the organic compound. An equally important class of substances, however, fix their hydrogen by addition. This class naturally comprises most of the unsaturated compounds, double and triple link, of both the fatty and aromatic series.

In the case of simple fatty substances, the addition of hydrogen is readily effected, the triple bond more so than the double, and copper is quite good enough as the catalyst.

The application of the method to compounds containing the aromatic nucleus is extremely wide, and includes some of the most important reactions it is able to accomplish. Carefully-reduced nickel is essential here, as well as delicate regulation of the temperature. Under these circumstances such classes of compounds as the hydrocarbons, the phenols, the aromatic amines and acids can be hydrogenised to the corresponding compounds of the cyclohexane series. In fact, the method comprises the principal one known for the preparation of saturated cyclic

compounds of this type. Thus, to take some simple examples, benzene yields cyclohexane, phenol gives cyclohexanol, and aniline a mixture of cyclohexylamine, dicyclohexylamine and cyclohexylaniline. As regards cyclohexane (hexahydrobenzene), this substance has recently been shown to possess possibilities in the direction of its utilisation as a motor fuel.

Naphthalene takes both four and ten, and anthracene four, eight, twelve, and fourteen, atoms of hydrogen, according to the temperature employed. These latter examples illustrate one of the most important developments of the method, viz., the possibility it affords, by reason of the varying activity of the available metals and the temperature limits at one's disposal, of tracing a reaction step by step—a process which adds considerably to our knowledge of the constitution of the bodies under treatment. In this manner, the method has been of the greatest service in determining the constitution of some of the members of the terpene and other series.

Of practical importance is the preparation of numerous artificial perfumes by the aid of this reaction. In addition, it permits of the production of cyclohexanol and *p*-methylcyclohexanol [9] (easily obtained from phenol and *p*-cresol respectively), which are used in the manufacture of isoprene and butadiene; and the method therefore may be destined to play an important part in the commercial synthesis of rubber—a problem which is at present occupying the attention of so many workers (see Chapter IX, sections 13 and 14).

10. The mechanism of these remarkable catalytic reactions can be explained in several ways. It may be that the passage of the hydrogen over the finely-divided metal induces its decomposition into the atomic or " nascent " state, or that the temporary

occlusion of the hydrogen upon the surface of the catalyst favours its interaction with the reducible body. The explanation put forward by Sabatier himself presupposes the formation of an intermediate unstable hydride upon the surface of the metallic catalyst, this hydride being capable of furnishing its hydrogen rapidly and in a suitable state to a substance which is able to utilise it. There might even be a series of hydrides formed, in which case the varying activity of the different metallic catalysts would find an explanation on the basis that the most powerful catalyst would be that capable of forming the greatest number of hydrides. Seeing that it was this idea which led him to initiate his prolific researches and has served as a guide throughout, the theory is worthy of consideration ; but the existence of such compounds as the theory postulates will have to be demonstrated in some independent way, nevertheless, before the uncertainty surrounding this explanation is removed.

(2) Catalytic Hydrogenation in the Liquid State.

(a) *Use of Finely-divided Metals at Ordinary Temperatures.*

11. Since the beginning of the nineteenth century it has been known that finely-divided platinum and palladium possess the property of occluding gases, particularly hydrogen, upon their surface. In the case of palladium, indeed, the effect is so marked that until recent years it was thought that one or more compounds was produced by union with the hydrogen. Instances are to be found in chemical literature in which this property has been taken advantage of for reduction purposes.

12. Comparatively recently a revival of the method has taken place, initiated primarily by Paal,[10]

who has proposed to utilise the still further increased area which obtains in a colloid. Colloidal solutions of platinum, palladium, osmium and iridium—of which the palladium hydrosol appears to possess the greatest value—were prepared by the action of some reducing agent, such as sodium protalbinate or lysalbinate, and later hydrazine, upon a solution of a salt of the respective metal. Large yields of the hydrogenation product were obtained by simply passing at the ordinary temperature a current of hydrogen through an agitated solution of the substance to be hydrogenated to which a little palladium hydrosol had been added.

In these reactions, however, the palladium hydrosol is converted into the inactive gel form by the procedure necessary for the isolation of the products, a factor which has rendered the process a costly one on account of the high price of colloidal palladium. The difficulty can be surmounted by precipitating the finely-divided metal upon inert substances devoid of anti-catalytic action, e.g., powdered nickel, magnesium, chalk, or kieselguhr.[11]

13. Skita has modified the method by using palladous chloride and gum arabic instead of colloidal palladium.[12] He also shows that the hydrogenation takes place more quickly and completely if the pressure of the hydrogen be somewhat increased. Later, the use of a protective colloid has been dispensed with.[13]

14. The use at ordinary temperatures of platinum which is in the finely-divided state of the so-called "black" and not in the colloidal state at all, has been demonstrated by Willstätter.[14] The method is capable of very extended application, for it is only necessary to dissolve the substance in some suitable solvent (if it is not itself a liquid), add a little platinum black, and pass hydrogen in whilst the liquid is under agitation.

15. The results by this method in its various modifications are comparable with those produced by the Sabatier process. The application, however, is not so general; for instance, by this method the benzene nucleus cannot be reduced. On the other hand, it can be applied to the reduction of compounds which are not sufficiently volatile, or are too easily decomposed, to be subjected to the Sabatier treatment. An example of this is the reduction of oleic to stearic acid at ordinary temperatures, and of vegetable oils to hard brittle products—an industrial process to be considered later in this chapter. Of course, the rapidity is nothing like so great as in the vapour process.

Two applications of the method are deserving of mention. The first is the hydrogenation of alkaloids,[15] whereby products are obtained which often possess more valuable medical properties than those of the parent substances. Morphine, brucine, strychnine, quinine, etc., yield their dihydro derivatives by treatment with hydrogen in the presence of a colloidal or finely-divided metal of the platinum group. The second application is that of the production of the leuco derivatives of the vat dyes,[16] e.g., of indigo white from indigo blue by this simple process, avoiding thereby contamination with the reducing agents employed in the older vats.

(b) *Use of Finely-divided Metals at Medium Temperatures.*

16. A general method for the preparation of aldehydes [17] by the direct reduction of acid chlorides is worthy of mention in this connection. By passing hydrogen through a boiling solution of the acid chloride in a hydrocarbon solvent in the presence of a catalyst until the escaping gas no longer contains hydrochloric acid, almost theoretical yields of the corresponding aldehyde can be obtained. The neces-

sity for using a boiling solution is rather a surprising feature, for it would have been expected that a low temperature would be desirable in order to prevent further reduction to the alcohol. Palladinised barium sulphate and finely-divided nickel prove good catalysts for the reaction. By this means benzoyl, butyryl, and stearyl chlorides have been converted into the corresponding aldehydes; whilst the method has also been applied technically to the manufacture of vanillin.[18]

(c) *Use of Metallic Oxides at High Temperatures and Pressures.*

17. Briefly stated, this method of hydrogenation,[19] associated with the name of Ipatiew, consists in bringing hydrogen at a pressure of at least 100 atmospheres into contact with the substance to be reduced in the presence of nickel oxide or other suitable oxide heated to temperatures above 250° in a specially-constructed steel tube. Iron and copper oxides display a similar catalytic activity.

It is unnecessary to mention any of the many accomplishments of the method, for it possesses no advantage over the preceding methods except in its application to the reduction of compounds which demand a high compression of hydrogen. Naturally, the danger attendant upon the process is a bar to its industrial development.

Hydrogenation of Oils.

18. Undoubtedly the most important application of the process of hydrogenation, and one which has made wonderful strides within recent years, is that which relates to the conversion of liquid vegetable oils, a cheap raw material, into the higher-priced solid varieties.

The preponderating constituent of most liquid ils is olein, the triglyceride of oleic acid; whereas

solid fats are composed largely of stearin or palmitin, the triglycerides of stearic and palmitic acids respectively. Oleic acid itself is a liquid: stearic and palmitic acids, on the contrary, being solids. A glance at the constitution of these acids reveals the important fact that the liquid acid is unsaturated, whilst the solid palmitic and stearic acids, the latter otherwise corresponding to oleic acid, are saturated bodies. The direct addition of hydrogen, therefore, should bring about the conversion of oleic acid into stearic acid, and the same applies of course to the glycerides of oleic and other unsaturated acids which should be transformed into the glycerides of the corresponding saturated acids. In other words, a liquid oil should be "hardened" by a process of hydrogenation. With the introduction of Sabatier's method so simple a solution of the problem first came within the bounds of possibility.

Previous processes of a chemical or electrical kind had not met with much industrial success. The only one which had proved of any value involved the treatment of oleic acid with strong sulphuric acid and the subsequent separation by distillation of the resulting oxystearic and other solid acids.

It was not long after the publication of the classical researches of Sabatier and his co-workers that patents were taken out by Normann [20] in England, and by Leprince and Siveke [21] in Germany, for processes based upon their principle. (It is interesting to note, however, that the former patent, so widely known by reason of its alleged fundamental character, was declared invalid in 1913 [22]). In these patents there was disclosed for the first time the possibility of the catalytic hydrogenation of substances in the *liquid* condition. From the technical standpoint, this discovery constituted a notable advance, for it permitted of the application of Sabatier's hydrogenation method, with its cleanliness and its perfect

control, to the treatment of substances, particularly oils, which cannot be vaporised without decomposition. Oil hydrogenation, as we have already seen, offered great commercial possibilities : and the above-mentioned discovery has led to their realisation.

19. Surveyed broadly, the methods now available for oil hardening can be classified under two main types :—

(1) The " batch " methods of Normann,[20] Wilbuschewitsch,[23] Testrup,[24] Kayser,[25] and others, in which hydrogen is bubbled through a mass of the oil charged with catalyst, or the mixture of oil and catalyst is sprayed in the presence of hydrogen, until the hardening has reached the desired stage.

(2) " Continuous " methods, as exemplified by the processes of Bedford,[26] and Ellis,[27] in which the oil, usually in the form of spray, is conducted along with hydrogen through or over the catalyst in a continuous manner.

In all cases, the effect desired is that of obtaining as intimate a contact as possible between the solid catalyst, the liquid oil, and the gaseous hydrogen.

20. The two essentials of the process are concerned with the production of an active catalyst and the problem of a cheap hydrogen supply.

21. With regard to the former, some kind of nickel is usually employed, because of its low cost and high efficiency. It may be in the form of powder or of extremely thin films or plates,[28] and may conveniently be supported upon some inert material,[29] preferably pulverulent, such as pumice or kieselguhr. The care involved in the preparation of the nickel catalyst has already been emphasised in connection with the work of Sabatier. As in that method, the most sensitive catalysts are obtained by reduction of the oxide at a low temperature, and when prepared,

access of air must be denied to them on account of their pyrophoric properties.

Other metals, notably platinum, cobalt, copper, and iron, can function as catalysts, though to a less degree than nickel. The rare-earth metals also furnish quite a number of useful catalysts, the most noteworthy being palladium.[11] In this connection, attention has already been directed to the work of Paal, Skita, and Willstätter (see sections 11—15). Though the addition of hydrogen takes place more quickly and at a lower temperature than with nickel, the high price of palladium precludes competition with the nickel method.

The superiority of the oxides of nickel over the metal itself has recently been urged by Bedford and Erdmann,[30] who find them to be more stable in the presence of oxygen-containing gases than catalytic nickel, less sensitive to the usual poisons, and to possess more strongly marked catalytic properties. Other oxides, such as cupric oxide and ferrous oxide, are capable of acting as catalysts, though not to the same extent as the nickel oxides.

Organic or inorganic salts of the catalytic metals, e.g., nickel formate [31] or borate,[32] are also stated to be of value catalytically. It is not certain, though, whether their activity is direct or is to be attributed to the formation of the metal or an oxide during the hydrogenation process. Indeed, opinion is still divided as to whether nickel monoxide is a catalyst *per se*, or whether its catalytic activity is dependent upon the formation of a suboxide or of the metal itself.

Since nickel carbonyl [33] is decomposed in heated oil to produce a suspension of very finely-divided metal, this compound provides a useful source of nickel catalyst, especially as, being volatile, it can be introduced into the oil along with the hydrogen. The liberation of the metal in what may be termed

the " nascent " state is said to be of considerable technical advantage.

As would be expected, care must be taken in all cases to exclude substances which, by poisoning the catalyst, reduce its life and efficiency. This applies not only to the catalyst itself, but also to the raw material under treatment and the hydrogen employed. In this respect, arsenic, sulphur, phosphorus, the halogens, antimony, tin, zinc, and lead, are the chief undesirables. As a rule, these substances exercise their deleterious influence whether present in the elemental condition or in the form of a compound; thus, a nickel catalyst would never be prepared from nickel sulphate. It might be mentioned here that the neglect of precautions against poisoning was the principal ground on which Normann's patent [20] was declared invalid. The difficulties attendant upon the complete exclusion of poisons is one of the reasons which militates against the use of water gas or coke-oven gas for the purposes of hydrogenation, though the cost of production of such gases, which contain some 40—50% of hydrogen, is very much lower than that of electrolytic hydrogen, or hydrogen of comparable purity. As regards enhancing the activity of the catalyst, the work of the Badische firm in this connection has already been referred to in section 4 of this chapter.

22. The problem of a cheap source of pure hydrogen is dealt with in Chapter V, sections 10—16.

23. Of the many forms of plant which have been designed for carrying out the fat-hardening operation, that of Wilbuschewitsch [34] is selected for description here. In this plant, shown diagrammatically in Fig. 11, the necessary degree of contact of the reacting materials is obtained by the use of one or more autoclaves, in which the hydrogen is made to contact with the oil both in bulk and in the spray condition. The mixture of oil with the requisite amount of

catalyst, obtained in the first instance from the mixer A, is delivered into each autoclave B through spraying devices C at the top, and in falling to the bottom the mixture comes into contact with a counter-current of hydrogen which has been injected in each case into the collected liquid in the conical lower portions D of the autoclaves. The hydrogen

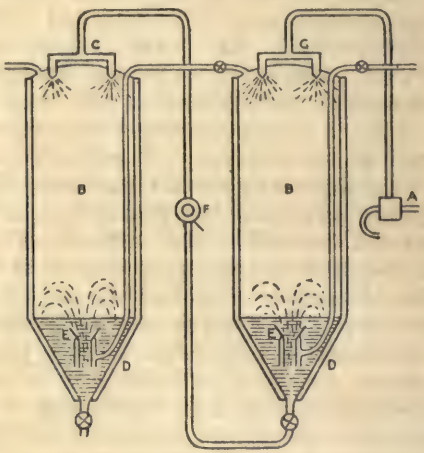

FIG. 11.

is introduced into the first autoclave at a pressure of about 9 atmospheres and emerges from the last at ordinary pressure. The autoclaves are provided with heating jackets in order that the temperature may be maintained at 100—160° according to the nature of the oil under treatment; also, devices E are fitted over each hydrogen admission nozzle to ensure as intimate a contact as possible with the oil mixture. After a certain period of treatment in the first autoclave, the oil is transferred by means of a pump F into the second autoclave, and so on, until a sample withdrawn from the last autoclave

gives the desired melting-point. The hardened oil is then removed and the catalyst separated from it by centrifugal treatment or by means of a filter press. The hydrogen not consumed may be returned to the first autoclave, after being purified by passage through caustic soda.

Other forms of apparatus employed are mainly mechanical variations of the one just considered, devised for the purpose of bringing the oil, the hydrogen, and the catalyst into effective contact. In all cases, the temperature of hydrogenation naturally depends upon the nature of the oil under treatment, the pressure of the hydrogen, and the catalyst employed. It usually falls between 150° and 200°. As a general rule, the hydrogen is introduced into the reaction chamber under pressure of a few atmospheres, but in some cases the hydrogen pressure has been increased to about 15 atmospheres,[35] it being then only necessary to raise the temperature to 100—150°. It is worthy of note that the Badische firm have recently advocated the use of pressures up to 120 atmospheres.[36]

24. The hardened oils resulting from the hydrogenation method are of great commercial utility. Since before the war plants in England, Germany, France, and Norway, have been engaged upon the production of solid fats for soap and candle making, using as raw materials such oils as cotton-seed oil, soya-bean oil, and linseed oil. Even in 1914, the weight of oil hardened in Europe by this means amounted to a quarter of a million tons.

A further application of the process to the manufacture of edible fats owes, if not its inception, at least its extensive development, to the shortage of butter and lard occasioned by the war. At first there was some objection to the use of fat substitutes prepared in this manner, based upon the suspicion that the presence of traces of the catalyst might be

injurious to health, or that cheap and unwholesome oils, such as certain fish oils, might be used as starting materials. These objections have been overcome, and now vast quantities of cotton-seed oil, soya-bean oil, cocoa-nut oil, etc., are hardened for the manufacture of margarine and compound lard, both of which are produced by mixing liquid oil with a proportion of the hardened variety. Attention ought to be directed, however, to the recent discovery [37] that the process of hardening vegetable oils destroys what are known as their " vitamines," the presence of which latter in food appears to be essential to the maintenance of health.

REFERENCES FOR CHAPTER VI.

[1] See " La Catalyse en Chimie Organique "—Sabatier (1913).
[2] B. P. 2306/1914 (Badische).
[3] B. P., 2011/1915 (Sabatier).
[4] D. R. P., 139457 (Senderens).
[5] B. P., 13149/1914 (Badische).
[6] Fr. P., 400656 (Sabatier).
[7] Sabatier, Int. Con. App. Chem., 1906, *3*, 188.
[8] B. P., 20488/1913 (Badische).
[9] See p. 316, " Rubber : its Production, Chemistry and Synthesis "—Dubosc and Luttringer (1918).
[10] *Ber.*, 1905, *38*, 1406.
[11] B. Ps., 5188/1911 and 16180/1914 (Paal).
[12] D. R. P., 230724 (Skita and Paal).
[13] B. P., 18996/1912 (Skita).
[14] *Ber.*, 1908, *41*, 1475.
[15] B. P., 3948/1912 (Vereinigte Chininfabriken Zimmer)
[16] B. P., 19848/1914 (Brochet).
[17] Rosenmund, *Ber.*, 1918, *51*, 585.
[18] B. P., 131161 (Matthews).
[19] Ipatiew, *J. Russ. Phys. Chem. Soc.*, 1906, *38*, 75.
[20] B. P., 1515/1903.
[21] D. R. P., 141029.
[22] R. P. C., 1913, *30*, 297.
[23] B. Ps., 30014/1910, 72/1912.
[24] B. P., 7726/1910.
[25] U. S. P., 1004035.
[26] B. P., 2520/1907.
[27] B. P., 24084/1912.
[28] B. P., 3344/1914 (Hagemann).
[29] B. P., 30282/1910 (Crosfield).

[30] *J. pr. Chem.*, 1913, *87*, 425; see also B. P., 29612/1910 (Bedford and Williams).
[31] B. P., 4665/1914 (Higgins).
[32] B. P., 7670/1914 (Müller).
[33] B. P., 18998/1912 (Lessing).
[34] B. P., 30014/1910.
[35] B. P., 7726/1910 (Testrup).
[36] B. P., 2307/1914.
[37] Report No. 38 of the Medical Research Committee (1919).

BIBLIOGRAPHY.

HYDROGENATION IN GENERAL :—
"Catalytic Hydrogenation and Reduction"—Maxted (1919).
"Reduktion und Hydrierung organischer Verbindungen" —Bauer (1918).
SABATIER'S METHOD :—
"La Catalyse en Chimie Organique"—Sabatier (1913).
SKITA'S METHOD :—
"Uber katalytische Reduktionen organischer Verbin dungen"—Skita (1912).
HYDROGENATION OF OILS :—
"Hydrogenation of Oils"—Ellis (1919).

CHAPTER VII.

Dehydrogenation, Oxidation, Hydration, Dehydration.

We turn now to a consideration of the catalytic dehydrogenation, oxidation, hydration, and dehydration of organic compounds.

Dehydrogenation.

1. When dealing in the last chapter with Sabatier's method of catalytic hydrogenation, attention was drawn to his explanation of the mechanism of the process on the assumption of the formation of intermediate unstable metallic hydrides. If this conception be correct, it would be anticipated that the catalysts employed in that process would be able to unite not only with hydrogen in the free state but also with hydrogen already in a state of combination. In other words, catalysts of hydrogenation should be catalysts of dehydrogenation too. Such is, in fact, found to be the case; and Sabatier [1] with his collaborators have thoroughly explored this field of research.

For example, the bodies produced by the hydrogenation of ring compounds tend to revert to the original substance if the temperature at which hydrogenation took place in the first instance be appreciably exceeded. Cyclohexane gives benzene: cyclohexanol regenerates phenol: piperidine reverts to pyridine: and so forth. The dehydrogenation may even be progressive, as in the case of dodecahydroanthracene, which loses its hydrogen in the

reverse manner of that in which the anthracene originally took hydrogen up.

Apart from the state of the catalyst, fairly high temperature is the essential condition. Since hydrogen is liberated, the reverse reaction sets in to some extent, but the concentration is not sufficient to produce a very serious diminution in the percentage yield. The most important of the applications of the method are briefly summarised below.

2. *Degradation of Hydrocarbons.*—All hydrocarbons, when submitted to a high temperature, are decomposed, with the partial formation of lower hydrocarbons, accompanied by dehydrogenation. In the presence of catalysts, the decomposition can be brought about at much lower temperatures, and consequently with somewhat better regulation than obtains in analogous pyrogenic decompositions. The loss of hydrogen appears to be accompanied by the scission of the hydrocarbon molecule into CH_3, CH_2, and CH groups, which then rearrange themselves into a further complex molecule whose empirical formula is poorer in hydrogen than that of the original hydrocarbon.

Not only cyclic hydrocarbons but also open-chain hydrocarbons undergo this degradation. Butylene, for instance, yields butadiene when heated in the presence of a catalyst.[2]

According to Sabatier, finely-divided and recently-reduced nickel displays the greatest activity in this connection. Cobalt is somewhat less active, iron begins to behave as a catalyst above 350°, and platinum as well as copper above about 400°. Traces of sulphur, arsenic and halogen compounds readily poison these catalysts. Another useful catalyst is aluminium chloride.

3. Whilst dealing with this subject, attention might be directed to the " cracking " of petroleum,[3] a process which consists in heating the heavier por-

tions of crude petroleum to a temperature sufficiently high to render the high-boiling hydrocarbons unstable and cause them to break down into lower-boiling hydrocarbons. The process is assuming greater and greater importance in view of the fact that the world's demand for petrol is increasing so rapidly that soon the " straight " distillation of crude oil may be unable to satisfy it.

Usually the cracking is effected by heating the oil under pressure, as in the Standard Oil Co.'s process,[4] which is extensively operated in America. Lately, though, it has been found that the transformation is facilitated by the use of catalysts. Nickel, iron, chromium, and other metals, preferably in the finely-divided state, appear to be of value in this respect, and the same applies to metallic oxides, such as copper, aluminium and iron oxides.

An example of a process involving the use of a catalyst is that of Hall,[5] in which the volatilised hydrocarbon, at a temperature of 600° and under a pressure of 5 atmospheres, is passed over a metal or oxide of the kind used in the hydrogenation of oils. By increasing the temperature and pressure to 750° and 7 atmospheres respectively, the process can be worked for the production of such aromatic hydrocarbons as benzene and toluene instead of petrol.[6] In further processes of a catalytic nature, the oil to be cracked is first mixed with steam and then brought into contact with hot wire spirals made of nickel or platinum,[7] or the mixture of oil and steam is passed through and over electrically-heated tubes of a catalytic metal.[8]

Other catalysts employed are the metallic haloids, particularly aluminium chloride, the Friedel-Crafts reagent. With a process of this type,[9] anhydrous aluminium chloride is added to the oil in a still and the whole is brought to boiling with stirring, fresh charges of oil being added at intervals to replace the petrol

which escapes through a condenser only cool enough to retain the higher-boiling fractions.

4. *Dehydrogenation of Alcohols.*—Long ago it was observed by Berthelot that the vapours of alcohol, when passed through a hot tube at 500°, suffer decomposition into ethylene and aldehyde. That is to say, under the influence of heat, there occurs both dehydration, or loss of water, and dehydrogenation, or loss of hydrogen. Subsequent experiments have shown that all primary alcohols decompose in this way when subjected to a temperature of about red heat. Secondary alcohols under similar conditions break down even more readily into unsaturated hydrocarbons and ketones.

By the aid of catalysts, the decomposition can be realised at much lower temperatures, a circumstance which is of value in view of the endothermicity of both reactions. And, what is of greater importance, Sabatier finds that one or other of the two reactions can be made to predominate, according to the nature of the catalyst selected.

Finely-divided metals, such as copper, cobalt, nickel, iron, platinum, and palladium, catalyse almost exclusively the dehydrogenation process. The same applies to a small number of oxides, chief among which are the lower oxides of manganese, tin, uranium, molybdenum, vanadium, and cadmium, though the activity of these is less than that of the metals. Other metallic oxides, on the contrary, such as thoria and alumina, are catalysts of dehydration, as will be seen when that phenomenon comes to be discussed (see section 18). And there still remains a large number of substances which can function to a varying degree as catalysts for both reactions.

5. As regards dehydrogenation, copper appears to be the catalyst *par excellence.* Nickel is ruled out on account of its violence, as pushing decomposition

too far; and the other catalysts mentioned above are much less advantageous than copper. It might be noted here that the Badische Fabrik [10] claim that the promoters they employ for hydrogenation catalysts (see Chapter VI, section 4) are also serviceable in the case of the catalysts of dehydrogenation processes.

Cyclic alcohols readily submit to this treatment. Isoborneol, for instance, is transformed into camphor [11] by passage over finely-divided copper at 300°; or camphor may be obtained from borneol or isoborneol by heating them without vaporisation in contact with a catalytic metal or oxide.[12] These reactions are of importance industrially in connection with the treatment of certain camphors which are sold cheaply on account of their large content of borneol. Similarly, a fatty or aromatic alcohol passed over copper at 200—300° gives a yield of at least 50% aldehyde or ketone. Thus, isopropyl alcohol gives acetone, and benzyl alcohol yields benzaldehyde.[13]

As already pointed out, the conditions are favourable to splitting because of the smallness of the hydrogen pressure. By working under reduced pressure, or what amounts to the same thing, diluting the alcohol vapour with an indifferent gas, the inverse reaction can be still further diminished.[13]

6. The most valuable of the industrial applications of this reaction is the preparation of formaldehyde from methyl alcohol. At the outset it may be remarked that the classification of the process as a dehydrogenation instead of an oxidation process is in accordance with recently-established opinion upon the theory of the subject.[14]

In Trillat's method,[15] which was the first proposed for large scale production, crude methyl alcohol was evaporated and passed, together with air aspirated in, through a vessel containing porous material maintained at a dull red heat. In modern plants, copper gauze is the usual contact material. Sometimes the

gauze is silver-coated; in fact, metallic couples in general, particularly those of copper or silver coated with platinum, are stated to possess great activity.[16] Silver itself and even gold have been suggested,[17] these metals of course being distributed over a supporting material. The alcohol is not now evaporated and mixed with air, but air is driven through wood spirit kept at a temperature suitable for saturation, and the mixture then passed into the catalyser, for which purpose scrubber or carburettor arrangements have been proposed.[18] In order to start the oxidiser without the application of external heat, small pellets of platinised asbestos or pumice, known as "ignition pills," are disposed in contact with the catalyst proper.[19]

Oxidation.

7. The most important processes involving catalytic oxidation are inorganic in character, and most of these have already been dealt with in Chapters II, III, IV, and V. Scattered throughout the domain of organic chemistry, nevertheless, are a number of catalytic reactions which can be classified under the general heading of oxidation processes, and these will now be discussed. Oxidation by electrolysis and oxidation by fermentation are dealt with in Chapter X.

8. *Colour Industry.*—One of the most valuable dyes in the whole range of synthetic colours is aniline black. This dye is produced on the fabric by the treatment of aniline hydrochloride ("aniline salt") with an oxidising agent, usually sodium chlorate, in the presence of certain metallic salts, such as sulphide of copper, which act as oxygen carriers. The most remarkable of these carriers is vanadium pentoxide. According to Witz,[20] the addition of one part of the oxide to the mixture of aniline salt and chlorate is sufficient to convert 270,000 parts of the aniline salt

into aniline black. After vanadium, in order of efficiency, come cerium, copper, uranium, and iron, employed in the form of various salts; whilst recently, it has been claimed that osmium tetroxide [21] possesses exceptional activity. Every one of these metals, it will be noticed, is capable of two degrees of oxidation.

In 1907 Green [22] patented a process for the production of aniline black in which the oxidation is effected by atmospheric oxygen instead of by the use of an oxidising agent, avoiding thereby any "tendering" or weakening of the fibre on which the dye is developed. The process depends upon the discovery that the addition of a small quantity of a paradiamine or a para-amidophenol to a mixture containing aniline and an oxygen carrier, such as a copper salt, greatly accelerates the atmospheric oxidation. The reaction is believed to be effected by the joint catalytic agency of the metallic carrier associated with an organic body of the type mentioned.

9. Fuchsine or magenta is another important dye whose preparation necessitates the use of a catalytic agent. Formerly arsenic acid was used for the oxidation of "aniline oil for red"—a mixture of about one part aniline with two parts *o* and *p* toluidines—but it has now been replaced by nitrobenzene, in which case metallic iron or ferrous chloride has to be added to the mixture to serve as an oxygen carrier. In the production, too, of methyl violet from dimethyl aniline, using chlorate as the oxidising medium, cupric chloride is always added on account of its catalytic properties.

10. The synthesis of indigo by Heumann's process,[23] which is worked by the Badische Anilin und Soda Fabrik, incorporates a splendid example of the catalytic acceleration of a reaction. The starting point of the synthesis is the oxidation of naphthalene to phthalic acid; and it was the accidental discovery

of the catalytic influence of mercury when fuming sulphuric acid is used [24]—the result of the breakage of a thermometer in one of the experimental tanks—which has rendered practicable the commercialisation of this elaborate synthesis.

As it happens, mercuric sulphate is much the most powerful catalyst for the process of oxidation by means of sulphuric acid. The sulphates of potassium and magnesium are inefficacious, whilst those of iron and nickel act but feebly. Only copper sulphate can replace mercuric sulphate, and then without advantage. A mixture of the two sulphates, nevertheless, displays an activity greater than the sum of both taken separately.[25] Mercury possesses a parallel catalytic effect in the Kjeldahl method for the estimation of nitrogen in an organic body.

11. Quite recently the aerial oxidation of naphthalene, and of other hydrocarbons in addition, has attracted attention. The catalysts employed are the oxides, or mixtures of the oxides, of metals of the fifth and sixth periodic groups. Of these metals vanadium appears to be the best, and molybdenum the next best.[26] Naphthalene and air, for instance, when passed over vanadium pentoxide at 450°, or over molybdenum trioxide at 500°, give a product which is mainly phthalic anhydride. In a similar way, anthracene can be oxidised to anthraquinone, toluene to benzaldehyde, and so on.[27]

12. *Preparation of Organic Acids.*—In the case of acetic acid, the most important acid in this connection, the consideration of its preparation is deferred until Chapter VIII (section 5). As for phthalic acid, its industrial production has just been referred to.

The production of oxalic acid is deserving of mention here, for though this acid is no longer prepared by the oxidation of sugar or starch by means of hot nitric acid, it is possible that this

method may be revived as a result of the discovery that the addition of a trace of vanadic oxide—1 gram per 1,000 grams of sugar—greatly accelerates the reaction.[28] Using this catalyst, the reaction proceeds at the ordinary temperature, and higher yields are obtained owing to the suppression of intermediate products, such as saccharic, mucic, and tartaric acids. The presence of molybdenum compounds is also stated to accelerate all reactions, including the one just mentioned, in which nitric acid is used as the oxidising agent.[29]

13. *Paint Industry.*—The hardening by drying of the oil which forms the most important constituent of paints, varnishes, etc., is such a slow process that it is necessary to add to the oil some material, known as a "siccative," in order to accelerate it.

It should first be noticed that the drying process *per se* is a catalytic one. Broadly speaking, hardening is the result of the absorption of oxygen from the air whereby intermediate products—usually considered to be peroxides—are formed, which catalyse the formation of still more of the products, the latter being ultimately changed into some indefinite compound. In the case of linseed oil, the final product is "linoxyn." The main reaction is therefore one of auto-catalysis.

That this is the case will be seen from Fig. 12, which represents the alteration in weight of a drying oil upon exposure to the air in thin films. The very shape of the curve, S-shaped, is typical of an auto-catalytic process. OA represents the "induction period" during which the weight of the oil remains fairly constant, whilst small quantities of peroxides, the natural driers, are being produced. At A the accumulation of peroxide is sufficient to effect a notable increase in the absorption of oxygen, and from that point the reaction proceeds with gradually

increasing rapidity until at B a maximum is reached. Beyond that point slackening occurs, consequent upon the decreasing concentration of the reacting substances. When a siccative is employed the induction period is reduced, but the S-shape of the curve is still maintained (see curve OCB). The siccative therefore functions as a pseudo-catalyst, since it accelerates the production of the auto-catalyst (see Chapter I, section 17).

14. As might be anticipated, the most powerful driers are themselves comparatively unstable peroxides. Manganese dioxide and red lead are those most

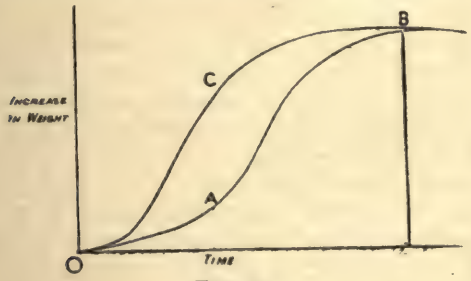

FIG. 12.

commonly employed, though many other metallic oxides possess some degree of activity. Cobalt compounds have recently been shown to display greater activity than those of either manganese or lead.[30] Some organic compounds, too, such as turpentine, which absorb oxygen with the probable formation of peroxides, possess a capacity for acting as driers.

The solid driers are now being replaced in the manufacture of boiled oil by liquid driers or " terebines," such as the resinates or linoleates of lead and manganese, which are soluble in both turpentine and linseed oil.[30] Whatever drier be employed, the

quantity necessary is small; in the case of manganese dioxide, for instance, 5 lbs. per ton of oil is all that is required.

In the manufacture of linoleum numerous attempts have been made to accelerate the slow hardening process by catalytic means, but in all cases the resulting product has been found inferior to that obtained from the unassisted oxidation of the linseed oil.

15. *Miscellaneous.*—Though, so far as is known, the whole of the formaldehyde used in industry is prepared in the manner described in section 6 of this chapter, the increasing application of this body has led to a consideration of other methods of production. In particular, the oxidation of methane has been suggested. In one process[31] this hydrocarbon, or any gas containing it, is to be mixed with an equal quantity of air and passed repeatedly through a tube containing granulated copper heated to 600°, the formaldehyde being removed after each cycle. In a recent modification[32] which aims at the removal of the difficulties associated with the control of the temperature, methane is fractionally oxidised at a temperature of only 150—220° in the presence of a metal or a metallic couple, such as copper or silver or both. A large excess of oxygen is employed in a cyclic process, the formaldehyde being removed by means of water.

16. As a last example, take the proposed preparation of camphor from borneol[33] or isoborneol[34] (compare the method described in section 5) by vaporising it in a current of oxygen and passing the mixture over a catalyst, e.g., spirals of copper or platinised asbestos.

Hydration.

17. Under this term are classified those reactions which comprise the direct addition of the elements

of water. Unsaturated hydrocarbons, acid anhydrides, amides, nitriles, lactones, etc., are capable of fixing water in a direct manner, and in certain cases the reaction is facilitated by the presence of a catalyst.

Of hydration processes the only important one which would concern us here is that of acetaldehyde, which forms the second step in the synthesis of alcohol; but as this reaction is dealt with in full in the next chapter, it is unnecessary to make further reference to it.

Dehydration.

18. So far as industrial chemistry is concerned, most of the products obtained by the general process of dehydration, or loss of the elements of water, result from a reaction in which either alcohols or acids or both are the main reagents involved.

(1) *Dehydration of Alcohols.*

19. With alcohols, loss of water can occur in two ways, either with the formation of an unsaturated hydrocarbon or of an ether. Ordinary alcohol, for instance, is dehydrated by concentrated sulphuric acid or syrupy phosphoric acid with the formation of ether if the temperature be not allowed to rise above 140°, or with the evolution of ethylene if the temperature conditions be maintained at 160—170°. In both cases, however, the acid plays the part of a desiccating agent and not that of a catalyst.

20. *Production of Ethylene Hydrocarbons.*—As true catalysts of dehydration, Sabatier—whose work on the catalysing power of oxides has already been referred to in section 4—has shown that, for the production of ethylene hydrocarbons from alcohols, there are no catalytic agents to compare with thoria, alumina, and the blue oxide of tungsten, when

employed at temperatures above 300°. Such a temperature is too high for the formation of ethers, since these latter are themselves then dehydrated.

If, therefore, the vapour of an alcohol be passed over thoria or similar catalytic material heated to 350—400° in an apparatus such as that shown in Fig. 10 (the hydrogen leading-in tube being of course suppressed), decomposition takes place with the production of an ethylenic hydrocarbon which can be condensed or collected in the gaseous state. Cyclohexanol, for instance, passed through a tube of platinum or silver at slight red heat gives a 40—50 % yield of butadiene.[35]

21. The reaction has been taken advantage of in the preparation of ethylene, the production of which comprises the first step in the manufacture of $\beta\beta_1$ dichlordiethylsulphide, extensively employed as "mustard gas" in the recent war. In the German method [36] of preparation, ethylene was obtained in 90 % yield by passing ethyl alcohol vapour over a catalyst of alumina contained in a copper tube heated in a bath of molten potassium nitrate to 400°. The British [37] employed coke impregnated with phosphoric acid as the catalyst; whereas in America [38] the process was modified by mixing steam with the alcohol vapour and passing the mixture over kaolin heated to 500—600°.

22. *Production of Ethers.*—The preparation of fatty ethers by dehydration of the corresponding alcohols is only possible in a small number of cases, mainly the lower primary alcohols. Secondary alcohols are usually, and tertiary alcohols invariably, transformed into the ethylenic hydrocarbon.

Phenols can be dehydrated in an analogous manner. If phenol vapour, for instance, be passed over thoria at 400°, diphenyl ether can be obtained to the extent of a 50 % yield. This reaction is already practised on an industrial scale and has considerably

reduced the price of diphenyl ether, which is employed in perfumery in large quantities as artificial essence of geranium. The phenol is liquefied and made to fall dropwise into the end of a heated inclined porcelain tube containing the thoria. The resulting mixture of phenol and its ether is separated by a single fractional distillation and the recovered phenol further treated.

Mixed ethers are obtainable by the use of a phenol and an alcohol. In this way, anisol and phenetol can conveniently be prepared. The products obtained by passing the vapours of β-naphthol with either methyl or ethyl alcohol over thoria comprise two perfumes (nerolin) which are extensively used for perfuming the cheaper grades of soap.

(2) *Dehydration of Acids.*

23. If an organic acid be heated to 420—450° in the presence of thoria, titanium oxide, zirconia, manganous oxide, ferrous oxide, cadmium oxide, or even chalk, water and carbon dioxide are eliminated with the production of a symmetrical ketone. By using a mixture of acids, say, benzoic acid and a fatty acid, mixed ketones can be obtained. Precipitated chalk, though not so effective as thoria, retains its activity even after it has become coated with carbonaceous products, but its use is only satisfactory in the case of the lower members of the fatty series and of benzoic acid.

Acetone is the most important body which has been prepared industrially by this reaction, but the account of its preparation is deferred until the next chapter (section 6).

(3) *Esterification.*

24. Esters are usually prepared by the interaction of an alcohol and an acid, a process known as esterification. Since water is eliminated, however,

the addition of such substances as concentrated sulphuric acid or anhydrous salts, which possess a strong affinity for water, in order to promote the reaction, renders it doubtful whether this reaction can be considered as catalytic.

For esterification in the gaseous state, which is undoubtedly a catalytic process, Sabatier has successfully employed some of the metallic oxides as reaction accelerators. Titanium oxide is stated to be the most advantageous for the production of fatty acid esters, and thoria for the esters of aromatic acids. Beryllium compounds,[39] too, have been advocated as catalysts in this connection. The catalyst may, of course, be suitably supported.[40]

(4) *Production of Amines and Thiols.*

25. Still other compounds may be catalytically prepared from alcohols by means of metallic oxides. Ammonia and the vapour of a primary alcohol, when directed over thoria at 250—350°, furnish a mixture of a primary and a secondary amine. Under the same conditions, a mixture of the vapour of a primary amine with ammonia yields a secondary amine. Mixed amines, as might be expected, may be prepared in a similar way. Secondary alcohols also produce amines, but not with such readiness as in the case of primary alcohols.

Primary and secondary alcohols, as well as phenols, can also be made to combine with sulphuretted hydrogen to produce good yields of thiols, if a mixture of this gas with the alcohol vapour be passed over thoria at 300—350°.

REFERENCES FOR CHAPTER VII.

[1] Sabatier, " La Catalyse en Chimie Organique " (1913).
[2] B. P., 17235/1912 (Perkin and Matthews).
[3] Lomax, Dunstan and Thole, *J. Inst. Pet. Tech.*, 1916, *3*, 37 (contains full bibliography).
[4] B. P., 29862/1912.

[5] First B. P., 17121/1913.
[6] B. P., 1594/1915 (Hall).
[7] B. P., 119485 (Adams).
[8] B. P., 20470/1913 (Valpy and Lucas).
[9] B. Ps., 17838/1913 (Gray), 22243/1914 (McAfee).
[10] B. P., 2306/1914.
[11] B. P., 17573/1906 (Goldsmith).
[12] B. P., 26708/1908 (Chemische Fabrik auf Aktien).
[13] B. P., 21367/1912 (Badische).
[14] See Wieland, *Ber.*, 1912, *45*, 484.
[15] Fr. P., 199919.
[16] B. P., 464/1914 (Hochstetter).
[17] See Fokin, *J. Russ. Phys. Chem. Soc.*, 1913, *45*, 286.
[18] D. R. P., 106495 (Klar and Schulze).
[19] Orloff, *J. Russ. Phys. Chem. Soc.*, 1907, *39*, 855, 1023, 1414, 1908, *40*, 796.
[20] See p. 56, "Aniline Black"—Noelting and Lehne (1909).
[21] B. P., 20593/1913 (Hofmann).
[22] B. P., 16189/1907.
[23] See "Indigo"—Brunck (1901).
[24] B. P., 18221/1896 (Badische).
[25] Bredig, *Zeitsch. physikal. Chem.*, 1903, *46*, 502.
[26] B. P., 119517 (Selden Co.).
[27] B. P., 119518 (Selden Co.).
[28] D. R. P., 183022 (Naumann).
[29] D. R. P., 228664 (Kinzlberger).
[30] See p. 73, "Chemistry of Linseed Oil"—Friend (1917).
[31] D. R. P., 109014 (Glock).
[32] D. R. P., 286731 (Verein für Chemische Industrie).
[33] B. P., 9008/1905 (Chemische Fabrik auf Aktien).
[34] B. P., 9550/1905 (Chemische Fabrik auf Aktien).
[35] B. P., 4076/1913 (Farbenfabriken).
[36] Norris, *J. Ind. Eng. Chem.*, 1919, *11*, 817.
[37] Pope, *J. Soc. Chem. Ind.*, 1919, *38*, 344 R.
[38] Dorsey, *J. Ind. Eng. Chem.*, 1919, *11*, 281.
[39] D. R. P., 261878 (Hauser and Klotz).
[40] B. P., 131088 (Boake, Roberts & Co.).

CHAPTER VIII.

Synthesis of Acetic Acid, Alcohol, and Allied Compounds.

1. Already in Chapter IV it has been mentioned that calcium carbide is manufactured in vast quantities for the production both of fertilisers and of nitric acid. Its utilisation, however, does not stop here, for in recent years a further wide field has been opened to it in its application to the synthesis of organic compounds, such as ethyl alcohol, acetic acid and acetone, which are of the utmost value in many industries.

Practically the whole of the reactions underlying these later developments are catalytic in character. They furnish, in fact, a number of striking illustrations of the advantages accruing to chemical industry by the modern application of the principles of catalysis.

By treatment with water, calcium carbide yields acetylene, and from acetylene by catalytic hydration acetaldehyde can be obtained. Then again, ethyl alcohol results from the catalytic hydrogenation of this acetaldehyde; or, if catalytic oxidation be resorted to, acetic acid may be prepared; from which, by further treatment involving catalytic dehydration, acetone is obtainable. Thus, it will be seen that by means of a series of reactions which can be represented diagrammatically as follows :—

$$Ca\,C_2 \rightarrow C_2H_2 \rightarrow CH_3\,CHO \rightarrow CH_3\,COOH \rightarrow CH_3\,CO\,CH_3$$

$$\downarrow$$

$$C_2H_5\,OH$$

it is possible to synthesise the three commercially-important chemical compounds already mentioned.

From these compounds, still others can be prepared, and by methods which are in general of a catalytic nature. The whole subject is as yet in an embryonic state, but it is possible even now to foresee extensive developments in the near future in the direction of the synthesis of organic products of increasing complexity.

Since all the reactions are closely interconnected, they are grouped together in this chapter for collective consideration.

Synthesis of Acetic Acid.

2. In view of the great industrial importance of acetic acid and of the necessarily localised character of its ordinary manufacture by wood distillation, it is not surprising that attempts have been made to replace this manufacture by synthetic methods. These efforts have met with considerable success, and during the recent war, both in Germany (where the process was first developed) and in the Allied countries, large amounts of acetic acid have been prepared by synthetic catalytic methods.

As pointed out above, the starting-point of the synthesis is calcium carbide, which is converted into acetic acid *viâ* the formation of acetylene and acetaldehyde.

3. *Preparation of Acetaldehyde.* — The process employed for the hydration of acetylene is based upon an observation by Erdmann and Köthner [1] that when acetylene is passed through boiling dilute sulphuric acid containing mercuric oxide acetaldehyde is formed. The technical application of this reaction, however, involves a number of difficulties, the most important of which appear to be:—(1) diminution in yield owing to the polymerising action of the

hot acid upon the aldehyde produced, giving crotonic aldehyde, resinous bodies, etc., (2) the deterioration of the mercury catalyst, which is gradually converted into an inactive slime containing organic mercury compounds and impurities, and (3) the selection of suitable materials for the apparatus to be employed.

As regards (1), the most obvious step is to reduce either the temperature or the strength of the acid, or to replace sulphuric acid by weaker acids, such as phosphoric acid, benzene sulphonic acid, etc., and the earliest attempts at improving the yield were in fact on these lines.[2] Recently, Dreyfus,[3] who has made an extensive study of the process, proposes a rigid control of the concentration and temperature conditions. The method which appears to be favoured, however, consists in passing the acetylene in very large excess through the catalysing liquid so that the stream of gas carries off the aldehyde as it is formed.[4]

Difficulty (2) above can be surmounted by adding oxidising agents to the catalytic liquid,[5] or by electrolytic oxidation in the reaction vessel.[6] The catalyst may be finally recovered by carbonising the sludge to metallic mercury.[7]

In connection with (3) above, the difficulty is that hot acid and mercury attack most metals, whilst earthenware is liable to break. Dreyfus [3] proposed to use lead vessels coated internally with lead sulphate, and subsequently [8] to employ the acid-resisting ferro-silicon alloys.

4. An interesting alternative synthesis [9] has also been described, in which the aqueous sulphuric acid mercury solution is replaced by a solution of mercuric oxide in glacial acetic acid containing a little sulphuric acid. The product obtained is the acetic ester of the hypothetical ethylidene glycol, viz., ethylidene diacetate

$$C_2H_2 + 2CH_3.COOH \rightarrow CH_3.CH\begin{matrix}O.COCH_3\\O.COCH_3\end{matrix}$$

which body, on heating to a fairly high temperature, with or without acids or acid salts, breaks down into a mixture of aldehyde and acetic anhydride.[10]

The high-temperature synthesis of acetaldehyde by passing acetylene and steam over various metallic oxides has also been studied,[11] but information is lacking as to whether this method has been established on a technical scale.

5. *Preparation of Acetic Acid.* — It has long been known that acetaldehyde is oxidised by air or oxygen to acetic acid. In the absence of a catalyst, however, the reaction is slow, though it may be accelerated by adding acetic acid at the start.[12] If a catalyst is to be used, two methods of operation are available—either the aldehyde vapours mixed with air or oxygen can be passed over the catalyst, or the reaction can be effected at a low temperature by passing air or oxygen into liquid aldehyde (b.p. 21°) containing the catalyst. Both methods have their drawbacks; the high temperature method is liable to losses due to over-oxidation of the aldehyde to carbon dioxide and water, while the low temperature method is not without danger, since low temperatures favour the production of peracetic acid,[13] a compound which decomposes with explosive violence.

Judging from the patent literature, however, the low temperature method appears to be the preferred one, using manganese compounds,[14] particularly the acetate,[15] as the catalyst, and employing the air or oxygen under pressure.[16] This method of preparation was successfully established during the war on a large scale at the Shawinigan Falls, Canada. It may be noted also that in Germany during the war the acetic acid synthesis was worked in conjunction with the manufacture of calcium cyanamide, the same raw material, calcium carbide, being used in both manufactures, while the oxygen obtained as a

by-product in the cyanamide process was used in the acetic acid production.

Products obtained Catalytically from Acetic Acid and Acetaldehyde.

The two compounds whose syntheses have just been described form the starting-materials for the preparation of a number of other organic products.

6. *From Acetic Acid.*—The most important compound in this connection is acetone, which at one period of the war was prepared in large quantities in Canada by a catalytic method in which acetic acid vapour is passed over lime as a catalyst at a temperature of 485°. Under peace conditions, however, it is thought that the method will not be able to compete financially with the ordinary process by the distillation of calcium acetate.

As the reaction is an old one,[17] modern developments have been concerned mainly with improving the efficiency of the catalyst. In one case the lime is distributed in the form of a covering over balls of heat-conducting material such as steel[18]; whilst in another manganese dioxide is suggested as the catalytic material, being employed in the form of lumps of pyrolusite.[19]

The preparation of acetic anhydride has already been referred to (see section 4).

7. *From Acetaldehyde.*—In the first place, acetaldehyde can be polymerised in several ways, depending upon the nature of the catalytic material employed. By treatment with small amounts of mineral acids, especially sulphuric acid, paraldehyde is produced; on the other hand, the addition of aqueous solutions or suspensions of alkalies, such as calcium or strontium oxide,[20] induces the so-called aldol condensation, which proceeds according to the equation :—

$$2CH_3 \cdot CHO = CH_3 \cdot CH(OH) \cdot CH_2 \cdot CHO.$$

Aldol may be used as a source of butadiene for synthetic rubber manufacture, and has also been proposed for the preparation of cellulose acetate solvents.

8. Again, if pure acetaldehyde be allowed to remain for some time in contact with a small quantity of finely-divided aluminium ethylate, direct conversion into ethyl acetate results.[21]

$$2CH_3 \cdot CHO = C_2H_5OOC \cdot CH_3.$$

The reaction should be a promising one, for the product is of comparative purity. The main difficulty appears to be associated with the slowness of the reaction, but efforts are being made to overcome this,[22] usually by the addition of a promoter to the catalyst.

9. Another compound of importance which can be derived from acetaldehyde is acetal. This body is obtained by mixing ethyl alcohol and acetaldehyde in the presence of hydrochloric acid and an amount of calcium chloride equivalent to about 10% by weight of the liquid.[23]

10. The last compound to be mentioned is ethyl alcohol itself which can be produced by the hydrogenation of acetaldehyde in a manner which it is now proposed to consider.

Synthesis of Alcohol.

11. In recent years the demand for oil fuel has increased at such a rate as to tax severely the world's natural resources of this commodity, particularly as regards the supply of the lower-boiling fractions which constitute petrol.

In Chapter VII (section 3) we have had occasion to notice the efforts which are being made in the direction of the conversion of high-boiling hydrocarbons into lower-boiling hydrocarbons by the process of "cracking"; but neither from this, nor from a more

complete extraction of benzol in coal-tar distillation, can be expected a sufficient supply of liquid fuel to counteract the forthcoming shortage. Some alternative supply, derived from new or supplementary raw materials, must be sought for and its possibilities investigated.

Attention has naturally been directed to alcohol in this connection, as providing the most promising solution to the problem. Already alcohol is prepared in large quantities by fermentation processes (see Chapter X), and this method appears capable of development by its extension to the treatment of other material than is at present employed, e.g., by the utilisation of wood-waste referred to in Chapter IX, (section 4). The most interesting proposal, however, is that for the chemical synthesis of alcohol. During the war, efforts in this direction were enormously stimulated, more especially in those countries such as the Central Empires, Switzerland, and Scandinavia, where the liquid fuel shortage was most acutely felt. That these efforts have attained a considerable measure of success can be gathered from the fact that the process has already been established on the industrial scale in both Germany and Switzerland, and that in the latter country the Lonza Electricity Works, which is operating the process, expects shortly to be in a position to satisfy the total alcohol requirements in Switzerland by this means. Considerable development of the synthetic process for the production of power alcohol can be confidently anticipated in other countries when the shortage and consequent increase in price of petrol permits of economic exploitation.

12. The reaction involved in the process is the hydrogenation of acetaldehyde by the classical method of Sabatier, to which such repeated reference has been made in the last few chapters. Acetaldehyde vapour admixed with hydrogen is passed over

a hydrogenating catalyst at a temperature of 140—180°, whereby even with a single passage through the catalytic material an 80% yield of alcohol is stated to be obtained. For the success of the process three conditions must be observed :—(1) the catalyst must be finely-divided nickel, prepared by the reduction of the oxide at a low temperature, (2) in order to minimise the effect of the reverse reaction it is necessary to employ a large excess of hydrogen and of course in a circulatory manner,[24] and (3) the temperature conditions must be carefully controlled so as to prevent as far as possible any diminution of the yield by the interference of catalytically-accelerated side reactions. Furthermore, the introduction of a fraction of a per cent. of oxygen has recently been claimed to reduce to negligible proportions the production of ether.[25]

REFERENCES FOR CHAPTER VIII.

1 *Zeitsch. anorg. Chem.*, 1898, *18*, 56.
2 B. Ps., 29073/1910 (Chemische Fabrik Griesheim Elektron); 6000/1913 (Consortium für Elektrochemische Industrie); 6527/1914 (Farbenfabriken).
3 B. P., 105064.
4 B. Ps., 16848/1913 and 17017/1913 (Consortium, &c.); 15669/1914 (Griesheim, &c.).
5 B. P., 24153/1914 (Farbwerke).
6 B. P., 130138 (Society of Chemical Industry, Basle).
7 B. P., 10140/1915 (Griesheim, &c.).
8 B. P., 115899.
9 B. P., 14246/1913 (Griesheim, &c.).
10 B. P., 23190/1914 (Bosnische Electricitaets-Actiengesellschaft).
11 B. Ps., 107584, 107585 (Deutsche Gold und Silber-Scheideanstalt); 109983 (Chemische Fabrik Rhenania).
12 B. Ps., 17424/1911 and 8076/1912 (Griesheim, &c.).
13 B. P., 16849/1913 (Consortium, &c.).
14 B. P., 17016/1913 (Consortium, &c.).
15 B. P., 7418/1914 (Consortium, &c.).
16 B. P., 10377/1914 (Farbwerke).
17 B. P., 2816/1898 (United Alkali Co.).
18 B. P., 138679 (Matheson).
19 B. P., 134144 (Société Anonyme des Acieries et Forges de Firminy).
20 B. P., 101636 (Grünstein).

[21] Tistschenko, *J. Russ. Phys. Chem. Soc.*, 1906, *38*, 355.
[22] B. Ps., 26825—6/1913 (Consortium, &c.); 1288/1915 (Farbwerke); 4887/1915 (Consortium, &c.).
[23] See B. P., 101428 (King and Mason).
[24] B. P., 120163 (Elektrizitätswerk Lonza).
[25] B. P., 134521 (Elektrizitätswerk Lonza).

BIBLIOGRAPHY.

Marshall, *Can. Chem. J.*, 1919, *3*, 254.
Matheson, *ibid.*, 258.

CHAPTER IX.

Hydrolysis, Saponification, Substitution, Polymerisation, Condensation.

A few more general reactions remain to be considered.

Hydrolysis.

1. The reactions now to be dealt with are those in which the elements of water are added to a complex, followed by resolution of the product into simpler substances. The compounds capable of this treatment can be roughly classified as esters: amides, oximes, and hydrazones: acyl derivatives: carbohydrates and glucosides: and lastly, polypeptides and proteins.

In the case of most of these substances, their hydrolysis can be catalytically accelerated. Indeed the hydrolysis of esters may be regarded as one of the best-known instances of catalysis, for the reaction being comparatively slow lends itself to a study of the phenomenon. Only the important of the above applications can be dealt with here.

2. *Hydrolysis of Esters.*—The simplest process, viz., hydrolysis by means of water, is an autocatalytic action, since the acid liberated functions as a catalyst. Under these circumstances the velocity of the reaction increases with the time. Naturally, such an unaided reaction is only possible in the case of the esters of comparatively strong acids, but if superheated steam be employed instead of water, the esters of even weak acids are affected. Thus, in the case of fats, which are natural glyceryl esters

of certain weak fatty acids, including stearic acid, their hydrolysis by means of superheated steam is used as a commercial method for the production of stearic acid for candles.

Esters can also be hydrolysed by water in the presence of finely-divided metals as catalysts. At 50°, e.g., platinum black accelerates the hydrolysis of ethyl butyrate. Far better results are obtainable by Sabatier's method,[1] in which a mixture of the ester vapour with excess of steam is passed over say titanium dioxide in the case of fatty acid esters, or over thoria for acids of the benzoic acid type, at a temperature of 280—300°.

The usual hydrolysing agents employed, however, are acids and alkalies, both of which are used to an enormous extent in the hydrolysis—or as it is then termed, the "saponification"—of fats. With this aspect of the problem it is proposed to deal separately at a later stage (see section 5).

3. *Hydrolysis of Carbohydrates and Glucosides.*—All di- and poly- saccharides can be hydrolysed in the presence of dilute mineral acids as catalysts, with the formation of mono-saccharides.

The hydrolysis of sucrose or cane sugar, for example, gives a mixture of dextrose and fructose, called "invert sugar." This reaction furnishes another of the best-known instances of catalytic reactions, for its course can be accurately followed by the change in optical rotatory power which accompanies the formation of the fructose. The process is of some importance industrially, for invert sugar is employed as a permissible addition in the manufacture of wine.

Of the poly-saccharides, starch is the most important to undergo hydrolysis by mineral acids, in this case with the final production of dextrose (glucose). The reaction underlies the technical manufacture of glucose. Starch from rice, potato, or maize is stirred

up with water and the mixture run into dilute sulphuric acid contained in a closed converter. The temperature is then raised by the injection of steam and the reaction continued until the hydrolysis is complete, when the product is run into tanks, the acid neutralised with chalk, and the clear solution containing the glucose finally evaporated under reduced pressure. In America, hydrochloric acid is the catalytic agent commonly employed.

In the case of glucosides their hydrolysis, too, can be fairly easily effected by the use of acids, though much less readily than when the appropriate enzyme is employed (see Chapter X, section 7).

4. *Hydrolysis of Cellulose.*—By reason of the possibility of a great saving in cost, the production of alcohol from wood-waste instead of from grain is finding technical application (see Chapter VIII, section 11). The first step in the process is the hydrolytic conversion of the cellulosic material into glucose, from which alcohol can then readily be obtained by fermentation in the ordinary way (see Chapter X).

Several processes have been devised for the disintegration by hydrolysis, but so far as is known, the only one in technical operation is that of Ewen and Tomlinson,[2] in which sulphuric acid is sprayed upon the wood-waste or sawdust in a rotary digester and steam then forced in under pressure of 7 atmospheres for a short time to raise the temperature and to produce an acid concentration not exceeding 1 %. After separating the sugar from the woody residue, the liquors are neutralised and the sugar fermentation carried out with the normal four-day period.

Saponification.

5. As previously mentioned, the term " saponification " refers only to a particular application of

hydrolysis, viz., the hydrolysis of fats. Since these latter bodies are made up of the glyceryl esters (glycerides) of certain fatty acids, particularly palmitic, stearic, and oleic acids, it follows that the reaction—which forms the basis of the soap industry—results in the formation of glycerol and the liberation of the fatty acids.

It must be realised in the first place that the reaction can proceed in the absence of a saponifying agent. Superheated steam has already been described as effective in this connection, but the temperature then becomes so high as to produce discoloration. For reasonable temperatures, the assistance of a saponifying agent must be called in. These agents may be either acidic or basic ; in the former instance, their behaviour is undoubtedly catalytic, but in the case of the bases, any catalytic activity they may possess is masked by the entry of the base into the reaction to produce the corresponding salt of the fatty acid. Only acid saponification will therefore be dealt with here.

6. The fat, which has previously been freed from moisture, is rapidly stirred for a period of 15—30 minutes in a special mixing machine with 3—4% sulphuric acid of 66° Bé. at a temperature of 90—120°. The completeness of the subsequent hydrolysis depends upon the strength of the acid, the temperature, and the period of contact, for unless these factors are carefully controlled, secondary reactions intervene with the formation of sulphur dioxide, acrolein, etc. After the required period has elapsed, the mixture is run into boiling water and agitated by steam to effect the hydrolytic change. The free fatty acids rise to the surface, leaving the glycerine behind in the dilute acid solution.

7. Of greater value than sulphuric acid for the promotion of this reaction are the fatty-sulpho-aromatic compounds discovered by Twitchell.[3] The

exact preparation of this catalyst is a trade secret, but as far as can be gathered it results from the interaction of an excess of sulphuric acid with a solution of oleic acid in some aromatic hydrocarbon, probably naphthalene. The compounds produced are themselves strong acids and have the property of dissolving both in fat and in water and of rendering them mutually soluble. Other compounds,[4] analogous with Twitchell's reagent, have been protected.

To saponify under these conditions, the fatty material, after having first been freed from all impurities by boiling with dilute sulphuric acid, is treated in wooden vessels for some time with half its weight of water and about 2% of the Twitchell reagent, the mixture being heated by steam coils and kept in agitation. The emulsion produced is then broken down by the addition of sulphuric acid, and after standing, the upper layer of fatty acid is drawn off.

Substitution.

8. *Friedel-Crafts Reaction.*—The well-known use of aluminium chloride for bringing about the substitution of the hydrogen of the benzene nucleus by alkyl groups was first made known by Friedel and Crafts [5] in 1877. Since that time, its application has been extended to the introduction into the aromatic nucleus of other groups, e.g., the preparation of aromatic ketones by the use of acid chlorides, of acids by carbonyl chloride, of aldehydes by a mixture of carbon monoxide and hydrochloric acid. In fact, the reaction now possesses an extraordinarily varied application in organic synthesis.

In all the above cases, the function of the aluminium chloride appears to be catalytic; and the accepted explanation of its action is based on the formation of complex intermediate compounds, some

of which have actually been isolated. Anhydrous ferric chloride brings about the same kind of result.

9. *Sandmeyer-Gattermann Reaction.*—The use of copper salts (Sandmeyer,[6] 1884) or of copper itself (Gattermann,[7] 1890) as catalysts for the replacement of the diazo group of aromatic compounds by chlorine, bromine, nitrile, nitro, and thiocyanate groups is so well known as to need no further description.

10. *Grignard Reaction.*—In the formation of the addition product of magnesium with an alkyl or aryl halide which comprises the Grignard reagent,[8] the reaction is found to be accelerated by the presence of a trace of iodine.

11. *Halogenation.*—The presence of iodine or of certain metallic halides greatly assists the process of halogenation. All the metals whose halides are efficacious prove to be of dual valency, so that no doubt exists as to their mode of action. In chlorination, for instance, the chlorides of antimony, iron, aluminium, and tin, or the metals themselves, prove very effective carriers, and the same applies to the elements phosphorus, sulphur, and iodine. For the introduction of bromine, the corresponding bromides are employed.

Chloracetic acid, for example, is prepared by passing chlorine into boiling acetic acid to which a little sulphur [9] or phosphorus has been added. Similarly, benzene [10] can readily be chlorinated in the ring at the ordinary temperature in the presence of a small amount of ferric chloride and finely-divided iron. For the introduction of halogen into the side chain, as in the preparation of benzyl chloride from toluene,[11] phosphorus trichloride furnishes a good catalyst, but the reaction requires the boiling of the toluene, preferably in the presence of sunlight, for a period of three to eight hours.

An important technical application of the use of a carrier is to be found in the preparation of carbon

tetrachloride, which is destined, by reason of its non-inflammability, to replace petroleum spirit, ether, etc., as a solvent. The method of preparation consists in the chlorination of carbon bisulphide. At the ordinary temperature chlorine and carbon bisulphide react but slightly, but in the presence of iodine or antimony pentachloride rapid formation of the tetrachloride ensues.[12]

12. *Sulphonation.*—Normally, catalysts are not employed in sulphonation processes. But in some instances they prove useful in determining the course of the reaction, as in the case of the sulphonation of anthraquinone, where the presence of a little mercuric sulphate favours the production of the α disulphonic acid instead of the usual β acid.[13]

Polymerisation.

13. *Synthesis of Rubber.*—Of the polymerisation processes, the most interesting, if not the most important, is the production of artificial rubber.[14]

If allowed to stand over some months, the unsaturated hydrocarbon isoprene, whose preparation has been referred to several times in the preceding chapters, slowly polymerises into a caoutchouc-like material—a fact first observed by Greville Williams [15] in 1860. By the addition of catalytic substances, however, the polymerisation period can be considerably reduced, especially if the temperature and pressure be raised in addition. Bouchardat [16] observed in 1875 the catalytic activity of hydrochloric acid in polymerising isoprene and was thus the first actually to synthesise caoutchouc; and since that time many other catalysts for the transformation not only of isoprene but also of its homologues, butadiene and dipropylene, have been discovered.

Of course the reaction is facilitated by raising the temperature and pressure; indeed, in the first

industrial synthesis of caoutchouc, butadiene or one of its homologues was heated in an autoclave for some days to a temperature of about 100°, either in the presence or absence of polymerising agents.[17]

14. The most advantageous catalytic agent appears to be metallic sodium, a fact which was discovered by Matthews [18] in 1910 and independently by Bayer & Co.[19] two months later. The great advantage associated with the use of sodium resides in the absence of any necessity for the employment of high temperature conditions over a prolonged period. Isoprene or one of its homologues is heated with sodium in an autoclave for three hours to a temperature of 35°, when a brown mass results, from which caoutchouc is precipitated by the addition of alcohol.

Of the other agents which have been advocated, the most noteworthy are acids (such as acetic acid), bases,[20] albuminoid substances,[21] sulphur,[22] and sulphur dioxide [23]; but none, so far as can be gathered, compare in efficiency with sodium, except perhaps acetic acid, the discovery of whose activity in this connection is coupled with the name of Harries. It might be observed that, according to the last-named investigator, sodium-condensed caoutchouc possesses a different structure from that which results from other condensation processes, though its physical characteristics are identical.

Unfortunately, though rubber has thus been synthesised in the laboratory, and to a small extent on the industrial scale, the cost of the manufacture of the isoprene and other hydrocarbons which form the starting materials for the polymerisation process is still too high to permit of synthetic rubber being marketed in competition with the natural product. Moreover, owing to the absence of small quantities of certain bodies presumably of a nitrogenous or resinous character, the synthesised material appears to be suitable only as a substitute for the harder and

less resilient rubbers. There are, therefore, no signs as yet that plantation rubber will share the fate of vegetable indigo.

15. *Synthetic Resins.*—What are known as "phenol-formaldehyde" compounds continue to attract a good deal of attention. These bodies are resinous amorphous products which are used in the manufacture of varnishes or lacquers, or which, after suitable treatment, are being used as substitutes for ebonite, celluloid, etc.

They are prepared by the condensation and subsequent polymerisation of formaldehyde and phenolic bodies in the presence of a suitable catalyst.[24] The reaction may proceed in the absence of a catalyst, but only under such unfavourable conditions—high temperature and long contact—as render the reaction impracticable for commercial purposes. The addition of acids or acid salts greatly accelerates the process, but their use is found to lead to the development of undesirable by-products.

Bases, on the other hand, serve as excellent catalysts, both at the condensation and polymerisation stages, and enable the reaction to proceed regularly and to be kept under control. Bakelite,[25] for example, is obtained by the action of an alkaline condensing agent in small quantity upon equal amounts of phenol and formaldehyde, the product being heated under pressure to 120—200°.

16. Quite recently, the technical possibilities of another class of artificial resins, viz., the coumarone resins, have been investigated. These resins result from the polymerisation of coumarone or indene, which are constituents of solvent naphtha or crude coal-tar naphtha, using such a condensing agent as aluminium chloride or sulphuric acid.[26]

17. *Aldehyde Polymerisation.*—Among aldehydes, the well known tendency to polymerisation is assisted by the presence of small quantities of basic or acidic

compounds, leading to the formation either of aldols or of polyaldehydes (see Chapter VIII, section 7).

18. *Acetylene Polymerisations.*—The polymerisation of acetylene to benzene by passage through a hot tube is well known to all students of chemistry. In the presence of certain other substances, and under catalytic conditions, acetylene is also able to effect a simultaneous combination and polymerisation.[27] Thus, if acetylene and sulphur vapour or sulphuretted hydrogen be passed over alumina at about 300°, thiophene is produced; whilst under similar conditions, acetylene and ammonia give pyridine bases.

Condensation.

19. The line of demarcation between condensation, polymerisation, and substitution reactions, as well as between condensation and dehydration reactions, is very difficult to define. Under this heading, however, are usually included such reactions as involve the union of two or more dissimilar molecules with or without the elimination of component elements.

20. When elimination takes place, certain additive substances called "condensing agents" are generally employed in order to assist in the removal of these elements. For instance, when water is to be eliminated, phosphorus pentoxide, anhydrous zinc chloride, or concentrated sulphuric acid is added to combine with the liberated water and so prevent the reverse reaction coming into play. In dealing with the subject of esterification (see Chapter VII, section 24), we had occasion to note reactions of this type. Similarly, when halogens are to be split off, metallic copper, silver, or sodium are employed; or when the elements of ammonia are to be removed, hydrochloric acid is added. Obviously, addition materials of this kind cannot be considered to function in a catalytic manner.

Where, however, the substance which is added to hasten the reaction is not of a nature to combine with the eliminated compound, and is not therefore employed in any but the smallest amounts, the effect of the addition can be regarded as genuinely catalytic. Such a function can be attributed to aluminium chloride and to copper or copper chloride respectively in the Friedel-Crafts and Sandmeyer-Gattermann reactions already referred to. The same applies to zinc chloride when the removal of hydrochloric acid is involved, or to ferric chloride in the case of the elimination of ammonia; and this accounts for the wide application in a catalytic capacity of both of these substances, as well as of aluminium chloride, in the manufacture of dyes, where condensations of this type are common.

When no elimination takes place, the necessity for the presence of a trace of a foreign body furnishes a clear case of catalysis. Ionone,[28] for instance, which is used as a substitute for essence of violets, is prepared from citral and acetone, using barium hydroxide as a condensing medium. And so examples might be multiplied.

Sufficient has been said, nevertheless, not only to indicate the diversity and extent of the application of catalysts in this field, but also to remove some of the prevailing confusion between the terms "catalyst" and "condensing agent."

REFERENCES FOR CHAPTER IX.

[1] See Sabatier, "La Catalyse en Chimie Organique" (1913).
[2] U. S. P., 1032392; see also U. S. Ps., 1032440-50 (Standard Alcohol Co.).
[3] B. P., 4741/1898.
[4] B. Ps., 27244/1911 and 17148/1914 (Petrow); 749/1912 (Vereinigte Chemische Werke Aktiengesellschaft).
[5] B. P., 4769/1877.
[6] *Ber.*, 1884, *17*, 1633.
[7] *Ber.*, 1890, *23*, 1218.
[8] *Compt. rend.*, 1900, *130*, 1322.

[9] B. P., 6031/1910 (United Alkali Co.).
[10] D. R. P., 219242 (Saccharinfabrik).
[11] See B. P., 17695/1902 (Marckwald).
[12] See B. P., 18990/1889 (Lever Bros.).
[13] B. P., 10242/1903 (Wedekind).
[14] See "Rubber: its Production, Chemistry and Synthesis"—Dubosc and Luttringer (1918).
[15] *Phil. Trans.*, 1860, *150*, 241.
[16] *Compt. rend.*, 1875, *80*, 1446.
[17] B. Ps., 15254/1910, 17734/1910, 25850/1910 (Farbenfabriken).
[18] B. P., 24790/1910.
[19] B. P., 1125/1911.
[20] B. P., 14281/1910 (Badische).
[21] B. P., 1124/1911 (Farbenfabriken).
[22] B. P., 10914/1911 (Badische).
[23] B. P., 17253/1914 (Heinemann).
[24] Baekeland, 8th Int. Con. App. Chem., 1912, *25*, 563; Lebach, *J. Soc. Chem. Ind.*, 1913, *32*, 559.
[25] B. Ps., 1921-2/1908, 21566/1908 (Baekeland).
[26] B. P., 117016 (Ellis).
[27] B. P., 109983 (Chemische Fabrik Rhenania).
[28] D. R. P., 73089 (Haarmann and Reimer).

CHAPTER X.

Enzymes, Electro-Chemistry, Vulcanisation Accelerators.

In this chapter, it is proposed to consider a few miscellaneous reactions which are of interest from the catalytic point of view.

Enzymes.

1. There are certain transformations, classified generally as fermentation processes, which were formerly considered to be induced by the presence of living organisms, that is to say, bacteria, moulds, etc., but are now attributed to the influence of the bodies, called "enzymes," or "ferments," which these organisms produce. Such reactions are of great interest from the present point of view, for they are closely allied to ordinary catalytic processes.

In the maintenance of animal life, the catalytic *rôle* of enzymes is of the utmost importance. Ptyalin of the saliva, for example, induces the transformation of insoluble starches and carbohydrates into soluble sugars; whilst pepsin of the gastric juice splits up insoluble complex albuminoid compounds into soluble simpler products, which are readily digested. Furthermore, the reverse processes, such as the production of fats from carbohydrates or the synthesis of proteins from simpler substances, are brought about in the animal body by the agency of enzymes.

2. Of extreme interest is the analogy between enzymes and ordinary catalysts as we know them.

In the first place, they increase the rate of what would otherwise be an extremely slow reaction. Moreover, a very small quantity of the enzyme will transform a relatively large amount of the fermentable substance. Then, again, the ferment emerges from the reaction unchanged, and except in cases where part of the ferment is removed by combination with the products, it emerges undiminished in quantity. As already mentioned, enzymes are also capable of inducing synthetic processes, which in itself is an indication of the reversibility of fermentation reactions. The activity of ferments, too, is greatly affected by the presence of other bodies; thus, certain substances, known as "activators," are essential for the action of particular enzymes: whilst enzymes in general are extremely liable to the paralysing influence of poisons, chief among which are hydrogen sulphide, hydrocyanic acid, iodine, and mercuric chloride, all of which will be recognised as common inhibitors of the kind of catalyst so far considered.

Enzymes differ from ordinary catalysts in two particulars. To begin with, they are characterised by a certain specificity of action, since each enzyme appears to exercise its activity exclusively upon a substance of a particular structural or even a particular stereochemical composition. The three disaccharides, sucrose, maltose, and lactose, for example, are hydrolysed by the same acids, whereas for enzymic hydrolysis each requires its own ferment. But, as pointed out in Chapter I (section 20), the ordinary type of catalyst is also more or less specific in its action, so that the difference is not so great as at first sight appears. More fundamental is the distinction based upon the fact that enzymes are destroyed by moderate heat, complete loss of activity being generally produced by raising the temperature even to 70°. However, enzymes are colloidal in their

physical nature, and this explains their behaviour under heat conditions.

It should be noticed, in passing, that no enzyme has as yet been isolated in a pure state. Their constitution, too, is entirely unknown; indeed, such appears to be the complexity of their character that it is likely to be some time before this problem is unravelled. On the whole, the above brief comparison of the characteristics of enzymes and catalysts almost justifies the consideration of physiological chemistry as a branch of catalysis.

3. Although it is possible in this chapter to give but the baldest outline of a very extended subject, some reference at least must be made to the more important industrial applications. These are mainly confined to the reactions of hydrolysis and oxidation.

4. The subjects of both enzymic hydrolysis and enzymic oxidation are intimately bound up with the production of alcohol. (For the production of alcohol by synthetic means, see Chapter VIII, section 10.) Alcohol is produced by the action of certain micro-organisms upon a simple sugar, these organisms being capable of oxidising or fermenting the sugar to carbon dioxide and alcohol. Although many bacteria can effect this transformation, quantitative decomposition is only obtained by the use of particular cultured moulds, grouped together as yeasts (*saccharomyces*), which in the course of their life-history produce the enzyme zymase. This enzyme is able to ferment a simple sugar like glucose, mannose, and lævulose, but cannot transform the higher saccharides, which must first undergo hydrolysis by means of a hydrolytic enzyme, e.g., maltase or invertase, also present in the yeast. With sacchariferous material, such as beet or molasses, therefore, all that is necessary is to add yeast in order to set up fermentation.

If, on the other hand, starchy or cellulosic materials be employed as the starting materials, they must first be degraded either by acid or enzymic hydrolysis into fermentable sugars—a process which is known as " saccharification."

With starch, saccharification is usually effected by treatment with the enzyme diastase. This enzyme is the active constituent of malt, which is prepared by allowing steeped barley to germinate for one to three weeks at a suitable temperature. The starchy materials, say potatoes, are first steamed and crushed, and the pulp then strired up in a vat with water and a little malt. When, after a few hours, the mash has acquired a sweetish taste (" sweet mash " or " wort ") due to the production of sugars, yeast is added to set up fermentation. The alcohol is finally separated from the fermented wort by distillation and rectification.

Technically, the two operations of the hydrolysis and fermentation of starch are sometimes combined into one, called the " amylo " process, by using a cultured fungus, either *amylomyces rouxii*[1] or *aspergillus oryzæ*,[2] which contains both enzymes. So far, however, their use has been limited to the treatment of corn mashes only.

In the case of a cellulosic material, such as sawdust, the hydrolysis is accomplished in the manner already described in Chapter IX, section 4, i.e., by treatment with acid under pressure, whereby the cellulose is transformed into sugars. Unfortunately, besides the fermentable hexoses, some unfermentable pentoses are formed, which detracts from the efficiency of the yield. After neutralisation, the subsequent treatment is the same as with starch.

5. Under the stimulus of war, two further bacteriological processes assumed first-rate importance. The first owes its development to the enormous demand for acetone in the Allied countries, as a

result of which every possible means of production of this valuable material was exploited to the full (see also Chapter VIII, section 6). The fermentation method is based upon the discovery by Fernbach [3] that sterilised carbohydrate material prepared from maize, potatoes, wood, etc., when subjected to the action of *bacillus butylicus*, can be converted into a mixture of acetone and butyl alcohol, instead of into the ethyl alcohol ordinarily produced. The treatment has to take place out of contact with the air and at a temperature of 25—40°; and the products are recovered either by distillation at the end of the operation or, if the fermentation be carried out *in vacuo*, the product can be withdrawn as formed. As the result of investigation, other suitable bacteria have been discovered, e.g., *bacillus macerans* by Bayer & Co.[4] and *bacillus granulobacter pectinovorum* by Weizmann.[5] During the war, acetone was manufactured in considerable quantities in both Great Britain and America by the Weizmann process; but with the advent of normal conditions, the process is not likely to be a commercial success, owing to the fact that the production of every part of acetone is accompanied by the formation of two parts of butyl alcohol.

In an interesting development, the yield of acetone is increased by adding to the fermenting mass acetic acid or a soluble acetate, which becomes converted by the bacteria or their enzymes.[6]

6. The second process, viz., the preparation of glycerol from sugar,[7] was developed to a very large extent in Germany during the war, when her supplies of fat became curtailed. It utilises the observation that the percentage of glycerine formed from sugar—normally only a minute amount—can be very appreciably increased if the fermentation be allowed to proceed in the presence of an alkaline substance, the proportions of the alkali being as large as will just

fail to inhibit the activity of the yeast. By the use of sodium sulphite, an alkaline agent which yeast can withstand in large proportions, 20—30% of the sugar present can be transformed into glycerol, the remaining products consisting of aldehyde, alcohol, and carbon dioxide.

7. The hydrolysis of glucosides by means of ferments finds technical application in the conversion of indican of the leaf of the indigo plant by means of indimulsin into glucose and indoxyl, in the degradation of tannins into glucose and such acids as tannic and ellagic acids by the agency of tannase, and so on.

8. Esters are also capable of hydrolysis. A recent application of this is the decomposition of fats by means of the lipase of castor seed [8]—a process which compares with the saponification of fats by alkalies, sulphuric acid, or steam, referred to in Chapter IX, section 5. The fat is melted in a pan with about half its weight of water and a little castor seed extract added. Fermentation is complete after six to eight hours, when the mass is heated to 100° to kill the enzyme and the product then separated.

9. The oxidation of ethyl alcohol to acetic acid, which is the reaction underlying the preparation of vinegar, is another industrial application of enzymic activity. Still further examples are to be found in the dairy industries, especially cheese-making, in bread-making, and in the treatment of sewage in water purification. For information with regard to any of the technical applications mentioned, the reader is referred to the voluminous literature which deals with these subjects.

Electro-Chemistry.

10. Electro-chemical methods for the preparation of chemical compounds are increasing in favour with

manufacturers, partly because of their cleanliness, but mainly by reason of their controllability. Not much has been done so far in the application of catalysis to electro-chemical reactions, but what has already materialised suggests that research in this direction might prove particularly fruitful.

11. *Reduction.*—The transference of the hydrogen generated *in situ* to the reducible body can be accelerated by the presence of a trace of certain foreign bodies. Thus, in the electro-chemical reduction of indigo, the addition of a little mercury, vanadium, iron, or titanium greatly favours the reduction process. Again, whereas quinone can ordinarily be reduced only as far as quinhydrone, in the presence of a trace of a titanium compound hydroquinone is produced.[9] Similarly, aniline can be prepared from nitrobenzene and benzidine from azobenzene in excellent yield, using a titanium carrier.

The material of the cathode is also considered to exert a catalytic effect, for there are substances which can be reduced much more readily at one cathode than at another, though the electro-chemical conditions may be equal in both cases. Nitrobenzene, for instance, is stated to be more easily reduced in acid solution at a lead[10] or zinc[11] than at a platinum cathode; whilst in alkaline solution, aromatic nitro compounds in general can be reduced to the corresponding amine and not to azo, azoxy or hydrazo compounds, provided a copper cathode be employed.[12]

12. *Oxidation.* — The use of a trace of an oxygen carrier in these instances is often of value for increasing the reaction velocity. For instance, the addition of 2% cerium sulphate[13] accelerates the oxidation of anthracene and naphthalene to the corresponding quinone. Vanadium compounds, too, are as useful in oxidation processes as in those of reduction. Aniline, for instance, is oxidised to benzo-

quinone in the presence of a vanadium salt;[14] and as we have already seen that benzoquinone can be reduced under catalytic conditions to hydroquinone, the employment of the two electro-chemical reactions affords a convenient method of preparation of hydroquinone from aniline. Vanadium also accelerates the oxidation of anthracene to anthraquinone. Other polyvalent metals whose salts have found application in this connection are uranium, thallium, manganese, and chromium.

The catalytic effect of the anodic material is not of much importance in oxidation processes.

Vulcanisation Accelerators.

13. The vulcanisation of india-rubber, discovered by Goodyear in 1839, consists in intimately mixing the rubber with a proportion of sulphur and then heating the mass to 140° for some time. With an average rubber mixing the time required for vulcanisation under these circumstances varies from one to three hours, and for vulcanite might be six hours or more.

In order to reduce this period it has long been the custom to add small quantities (up to 5%) of certain metallic oxides, notably the oxides of lead, magnesium, and calcium; but the use of these "sulphur carriers" has been restricted to the manufacture of goods of lower grade quality only, since the effect of their addition, apart from being catalytic, often proves undesirable.

14. Within recent years, however, a number of organic accelerators have been discovered of such powerful catalytic effect as to be of the greatest value in the rubber industry. The first to be brought to light was piperidine, whose use was patented by Bayer & Co.[15] in 1912; and a little later[16] they

claimed the employment as activators of all organic bases whose dissociation constant exceeds 1×10^{-8}.

Many other organic compounds appear to possess the same curious property. Peachey [17] showed in 1914 that the nitroso derivatives of certain bases, particularly dimethylaniline, methylaniline, and diphenylamine, when employed in quantities of 0·3 to 0·5%, reduce the time of vulcanisation to one-third of that normally required. Other nitroso compounds, destitute of basic properties, such as nitrosophenol [18] or even nitrosobenzene,[19] also act as accelerators. Indeed, during the last year or two, a whole host of substances, mostly of a basic character, have been stated to be applicable for this purpose.[20]

The use of these organic accelerators appears to be free from the disadvantages attendant upon the use of litharge, lime or magnesia, and as they have already been introduced with success into works practice, it would appear likely that their use will become general in future.

REFERENCES FOR CHAPTER X.

[1] B. Ps., 1155/1897, 19858/1897 (Collette and Boidin).
[2] B. Ps., 17374/1891, 17277/1894 (Takamine).
[3] B. P., 21073/1912.
[4] B. P., 14371/1914.
[5] B. P., 4845/1915.
[6] B. P., 128403 (Desborough).
[7] *J. Soc. Chem. Ind.*, 1919, *38*, 287 R.; see also B. P., 133374 (Eoff).
[8] See p. 42, "Glycerine"—Koppe (1915).
[9] B. P., 15700/1903 (Farbwerke).
[10] Löb, *Zeitsch. Elektrochem.*, 1898, *4*, 430.
[11] Elbs, *ibid.*, 1901, *7*, 589.
[12] B. P., 25100/1901 (Boehringer).
[13] B. P., 19178/1902 (Farbwerke).
[14] B. P., 18042/1904 (Farbwerke).
[15] B. P., 11530/1913.
[16] B. P., 12661/1914.
[17] B. Ps., 4263/1914, 10833/1914.

[18] B. P., 101819 (Peachey).
[19] B. P., 136716 (Peachey).
[20] See Twiss and Brazier, *J. Soc. Chem. Ind.* 1920, *39*, 125.

BIBLIOGRAPHY.

ENZYMES :—
" Biochemical Catalysts in Life and Industry "—Effront (1917).

ELECTRO-CHEMISTRY :—
" Manufacture of Chemicals by Electrolysis "—Hale (1919).

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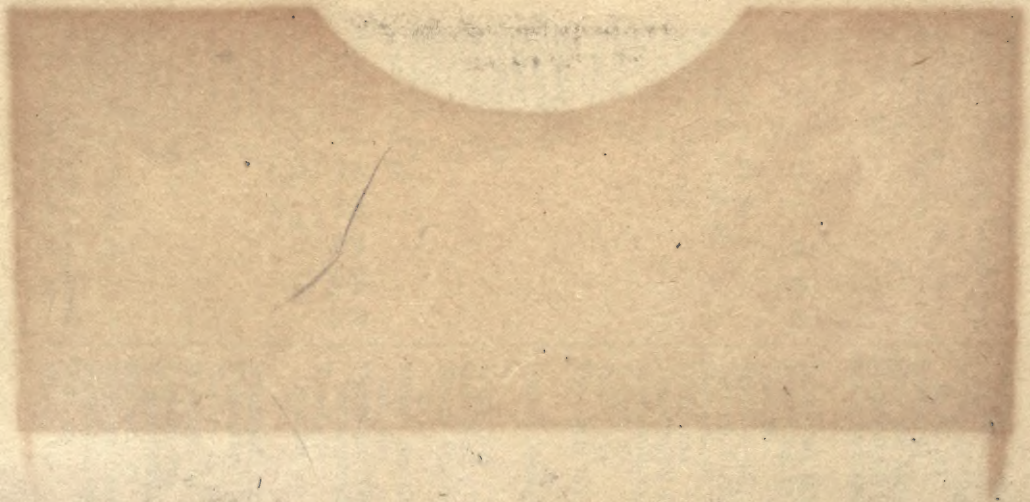

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